Evaluation of Waste Tire Devulcanization Technologies

December 2004

Produced under contract by:

CalRecovery, Inc.

Zero Waste—You Make It Happen!

Disclaimer: This report to the Board was produced under contract by CalRecovery, Inc. The statements and conclusions contained in this report are those of the contractor and not necessarily those of the California Integrated Waste Management Board, its employees, or the State of California and should not be cited or quoted as official Board policy or direction.

The State makes no warranty, expressed or implied, and assumes no liability for the information contained in the succeeding text. Any mention of commercial products or processes shall not be construed as an endorsement of such products or processes.

Table of Contents

Acknowledgements

Executive Summary

This report presents the results of the evaluation of waste tire devulcanization technologies performed by CalRecovery, Inc. under contract with the California Integrated Waste Management Board.

Devulcanization is a potential method of recycling waste tire rubber. Devulcanized rubber is a highly valued form of waste rubber since devulcanized material can be revulcanized into useful products.

Approximately 25 potential devulcanization technology researchers and developers were identified throughout the world and North America, including three in California. However, only a very small number of devulcanization systems are now operating. These are primarily small-capacity systems, which are devulcanizing natural or synthetic rubbers (as opposed to devulcanizing the mixture of rubbers recovered from waste tires).

The general types of devulcanization technologies identified and analyzed in the study are shown below.

Technology	Basis of Processing	Zone of Reaction
Chemical	Chemicals/chemical reactions	Surface of particles
Ultrasonic	Ultrasonic waves	Throughout particles
Microwave	Microwaves	Throughout particles
Biological	Microorganisms	Surface of particles
Other	Mechanical Steam	Surface of particles

Key Findings

- Reliable information and data on devulcanization of waste tire rubber are difficult to obtain due to proprietary claims, efforts to hide poor or infeasible process performance and product quality, and the limited number of technology researchers and developers and of peer-reviewed data. Reliable data relating waste tire characteristics, devulcanized rubber quality, end product performance, and production costs is scarce.

- Only a very small number of low-capacity devulcanization systems are operating in the United States (at approximately 100 lb/hr, all R&D scale, mechanical, or ultrasonic). No proven commercial capacity units could be found that are currently devulcanizing waste tires, for example, at 1000 lb/hr or greater. The likely reasons include insufficient product quality and high costs of production.

- In terms of the potential of producing high-quality devulcanized rubbers (for example, high strength), the best technology appears to be ultrasonic, based on the current state of the art.

- Devulcanization of single rubbers has much more history than that of multi-rubber mixtures such as waste tires. Only a few companies devulcanize single formulation rubber as a result of captive conversion or merchant scrap recovery from manufacturing. The production of devulcanized rubber from home manufacturing scrap ranges from 100 to 200 million pounds annually, which represents about 1 to 2 percent of total U.S. rubber consumption. The largest volume devulcanization activity supports the domestic tire and rubber companies. Examples

of devulcanized single-product rubber applications are tire bladders, seat spring covers, various molded goods, and foam crack sealer. The quality of devulcanized single rubbers is higher than that of devulcanized multiple rubbers.

- Markets and uses for devulcanized waste tire rubber are generally scarce, opportunistic, and lack history and standards. Based upon limited market history and potential, devulcanized tire rubber would be expected to find uses in molded goods, binders for plastics, and applications needing a better surface finish. Examples of product areas are footwear soles, rubber sheeting, car mats, and inner liner compounds. Potential uses of devulcanized rubber of especially high quality and performance could include tread and sidewalls of tires; this level of high quality has not been demonstrated. Devulcanization that depends on surface devulcanization technologies (for example, chemical and mechanical) appears destined in the near term to produce low- or medium-quality devulcanized rubber material.

- The estimated cost for producing devulcanized materials from waste tires is $0.7 to $1.2/lb ± 30 percent, including the cost of crumb rubber feedstock. This range of production costs is significantly greater than that of virgin rubbers.

- All things considered under current and likely near-term future conditions, devulcanization faces an uphill struggle to be competitive with virgin rubber.

Key Research Needs

- Sponsor waste tire devulcanization projects that secure reliable and comprehensive data that document and relate feedstock characteristics, operating conditions, environmental impacts, cost, and type and quality of products, with the objective of producing high-quality devulcanized rubber.

- Identify methods that reduce the cost of production, while at the same time yielding high-quality devulcanized rubber and/or manufactured compounds or end products.

Chapter 1. Introduction

Devulcanization of rubber has a long history, but renewed interest in the subject has arisen during the past five to ten years due to increased regulatory and public concern for properly managing waste tires.

Devulcanization is a potential method of recycling waste tire rubber. As its name implies, in the process of devulcanization, the structure of the vulcanized waste rubber is modified. The resulting material can be revulcanized or transformed into useful products (see complete definition on page 4). Devulcanized rubber is a highly valued form of waste rubber.

The evaluation begins with a review of research and development as determined by a search of the literature. Subsequently, types of devulcanization technologies are described and analyzed in terms of technical aspects, cost, market situation, and environmental considerations. Barriers to waste tire devulcanization are then discussed, along with potential methods of resolving them. Lastly, major conclusions and recommendations of the study are offered at the end of the report.

An overriding consideration of the evaluation is devulcanization of waste tire rubber, as opposed to single types of rubber. The reason is that tires are composed of mixtures of multiple rubbers (as well as other constituents), which renders devulcanization of waste tires much more challenging than that of single rubbers.

Chapter 2. Status of Research and Development for Devulcanization Technologies

Introduction

Methods of devulcanizing elastomers (or rubber) have been researched almost since the time of the discovery of the rubber/sulfur vulcanizing process by Charles Goodyear in 1839. Many papers have been published on subjects relevant to devulcanization. Additionally, a number of patents have been issued on topics concerning devulcanization processes. The discussion below describes the results of a review of the status of research and development performed in the area of devulcanization.

Devulcanization has been applied to different types of elastomers. The purpose of this analysis is to describe the development of devulcanization processes in general and to relate those developments to the potential for devulcanizing waste tire rubber. Waste tires are composed of a number of different constituents, including vulcanized natural and synthetic rubber compounds, steel, fiber, and other materials. The status of devulcanization must also be measured against the potential uses of devulcanized waste tire rubber and the ability of the devulcanization processes to achieve yields and quality of rubber necessary to make devulcanization feasible.

Definitions

There is some discrepancy in the literature among key terms that will be used in this analysis and in their definitions. In the discussion on research and development of devulcanization, CalRecovery uses the following terms:

Vulcanization is the thermo-chemical process that incorporates sulfur and sulfur crosslinks into a mixture of rubber molecules in order to provide the elasticity and other properties that are desired in manufactured rubber products. In the process, sulfur atoms are chemically bonded to the carbon molecules of rubber molecules and serve as crosslinks (chemical bonds) between the sulfidic rubber molecules. The vulcanization process is irreversible at standard atmospheric conditions of temperature and pressure. The vulcanization process also uses primary and secondary accelerators, typically sulfur-containing organic compounds and activators such as zinc oxide and stearic acid.

Reclaiming is a procedure in which scrap tire rubber or vulcanized rubber waste is converted—using mechanical and thermal energy and chemicals—into a state in which it can be mixed, processed, and vulcanized again. The principle of the process is devulcanization (Franta, 1989). Historically and practically, in the concept of rubber reclaiming, devulcanization consists of the cleavage of intermolecular bonds of the chemical network, such as carbon-sulfur (C-S) and/or sulfur-sulfur (S-S) bonds, with further shortening of the chains also occurring (Rader, 1995). This description of devulcanization is different than that given below, which is limited to chemical interactions involving sulfur atoms.

Devulcanization is the process of cleaving the monosulfidic, disulfidic, and polysulfidic crosslinks (carbon-sulfur or sulfur-sulfur bonds) of vulcanized rubber. Ideally, devulcanized rubber can be revulcanized with or without the use of other compounds. The different types of devulcanization processes also modify other properties of the rubbers. These processes cause diminution of some properties over those of the parent rubber. Ideally, devulcanization would

4

yield a product that could serve as a substitute for virgin rubber, both in terms of properties and in terms of cost of manufacture.

Methodology

In order to establish the status of research and development for devulcanization technologies, CalRecovery used a number of resources. CalRecovery could not rely solely on the peer-reviewed literature to provide the greatest capture of information covering devulcanization of sulfur-cured rubber or of waste tires. The project team consulted the following sources, both in North America and internationally, listed below:

- Popular and peer-reviewed literature.

- Waste tire processors.

- Patents.

- Tire manufacturers.

- State and federal agencies.

- Universities and research institutes.

- Associations and organizations.

- Website search engines.

- Subconsultants of CalRecovery.

Based upon the data and information collected among the various sources, the research and development status of devulcanization was determined for a variety of technologies and processes.

Composition of Waste Tires

A typical tire compound contains the following constituents:

- Natural and synthetic rubber.

- Reinforcing fillers.

- Oils.

- Antioxidants.

- Zinc oxide.

- Accelerators.

- Sulfur.

Grinding and Pulverization Technologies

Use of waste rubber in a vulcanized state most often requires reduction of particle size or increase in surface area. One of the widely used methods for doing this with scrap rubbers and wastes is a grinding process.

The three current methods of grinding waste rubber are: (1) ambient grinding, (2) cryogenic grinding, and (3) wet-ambient grinding (Harshaft, 1972). Vulcanized scrap rubber is first reduced

to a 2 x 2 inch or 1 x 1 inch chip. Then a magnetic separator and a fiber separator (cyclone) remove all of the steel and polyester fragments. The waste rubber can then be further reduced using an ambient ground mill, or it can be ground into fine particles while frozen using cryogenic grinding (Klingensmith & Baranwal, 1998).

One method for obtaining fine-mesh rubber is cooling scrap tires in liquid nitrogen below their glass transition temperature and then pulverizing the brittle material in a grinder. Cryogenically-ground rubber has a fine particle size, varying from 30 to 100 mesh. Except for inexpensive rubbers such as tire rubbers, the process is not economical because of the substantial quantities of expensive liquid nitrogen or other cryogenic liquids needed to freeze the rubber (LaGrone, 1986).

However, the process may be economical for expensive rubbers such as fluorocarbon rubbers. Little or no heat is generated in the process, resulting in less degradation of the rubber. In addition, the most significant feature of the process is that almost all fiber or steel is liberated from the rubber, resulting in a yield of usable product and little loss of rubber (Klingensmith & Baranwal, 1998).

Ambient mechanical size reduction by chopping and grinding often uses a conventional high-powered rubber mill set at close nip. The vulcanized rubber is sheared and ground into small particles. Using this relatively inexpensive method, it is common to produce 10- to 30-mesh material, which is a relatively large crumb.

In addition, multiple grinder passes can be used to further reduce the particle size. Ambient grinding produces an irregularly shaped particle with many small hair-like appendages that attach to the virgin rubber matrix, producing an intimate bonded mixture (Szilard, 1973). The lower particle limit for the ambient grind process is the production of 40-mesh material. The process, however, generates a significant amount of heat. Excess heat can degrade the rubber. If the rubber is not cooled properly, combustion can occur upon storage.

A process using a wet grinding method to achieve a crumb fineness of approximately 200 mesh has been reported (Lynch & LaGrone, 1986). Wet or solution process grinding can yield a very small particle size, ranging from 400 to 500 mesh. The advantage of fine particle wet ground rubber is that it allows good processing, producing relatively smooth extrudates and calendered sheets (Lynch & LaGrone, 1986).

Grinding processes for tire rubber are well developed. They are widely used for recycling of tire rubbers and rubber wastes. Also, industrial machines are available for breakup and separation of rubber from steel, cord, and fabrics that are present in tires. High industrial rates for production of tire rubber crumbs have been achieved.

Pulverization techniques for rubbers are also being developed based on the concept of polymer pulverization that was originally proposed for plastics. The process manufactures polymer powder using a twin-screw extruder, imposing compressive shear on the polymer at specific temperatures that depend on the polymer (Enikolopian, 1985).

Based on this method, the solid-state shear extrusion pulverization method of rubber waste using a twin-screw extruder and a single-screw extruder has also been proposed [(Khait & Torkelson, 1999; Khait, 1994) and (Bilgili, et al., 2000; Bilgili, et al., 1999; Bilgili, et al., 2001, pp. 265–276; Bilgili, et al., 2001, pp. 277–289), respectively]. The pulverized rubber particles were fluffy and exhibited a unique elongated shape.

In solid-state pulverization, the rubber granulates are fed into the hopper of the extruder and conveyed into the compression zone, where they are subjected to high compressive shear. Under simultaneous action of this compressive shear and torsion due to the screw rotation, the

granulates are pulverized. They emerge from the pulverization zone as a rubber powder with smaller particle size. Surface oxidation of the rubber particles and initiation of agglomeration of a fraction of the produced particles may occur. The particles produced exhibit irregular shapes with rough surfaces and have a porous structure. The particles obtained in this process can be molded into products after exposure to high heat and high pressure for a period of at least one hour (Arastoopour, et al., 1999; Bilgili, et al., 2003).

The pulverization technologies have been developed on laboratory scale only. Currently, efforts are underway to develop machines for a large-scale production of pulverized tire rubbers. During this process, the tire rubber is apparently only slightly devulcanized, mainly in the proximity of the surface layer of rubber particles. The main disadvantage of the technology is the generation of tremendous amounts of heat due to compression and shearing actions in the pulverization zone that are difficult to control.

It should be noted that all such grinding processes produce little chemical change in the rubber beyond the degradation that occurs as a result of exposure to heat during the process. The ground rubber thus produced functions essentially as a filler when compounded with virgin rubber. The one advantage it may have over other fillers, such as carbon black or clays, is that it will be able to chemically bond with the new rubber to some extent in the vulcanization process. Used alone, its applications are limited to products requiring relatively low physical and mechanical properties.

Types of Devulcanization Technologies Identified

A search of the literature and patents was performed to determine the status of devulcanization technology and processes. In summary, the information is grouped into the following categories:

1. Chemical.

2. Ultrasonic.

3. Microwave.

4. Biological.

5. Other.

Results

The results of the status evaluation are discussed below under each of the respective categories of devulcanization processes.

Chemical

Organic Solvent Only

One type of chemical method proposed (Hunt & Kovalak, 1999) is based on the use of 2-butanol solvent as a devulcanizing agent for sulfur-cured rubber under high temperature and pressure. The authors of the study claim that the molecular weight of the rubber is retained and its microstructure is not significantly altered during the devulcanization process. However, the process is extremely slow and requires separation of the devulcanized rubber from the solvent. The process is applicable to devulcanization of finely ground tire rubber, but so far it has been carried out only on a very small laboratory scale.

Another type of chemical technology (Benko & Beers, April 2002; Benko & Beers, May 2002; Benko & Beers, October 2002) uses a solvent to treat (devulcanize) the surface of crumb rubber

particles of sizes within about 20 to 325 mesh. This is similar to the proposal by Hunt and Kovalak. The process is carried out at a temperature range between 150° to 300°C (300° to 575°F), at a pressure of at least 3.4 Mega Pascals (MPa), in the presence of solvent selected from the group consisting of alcohols and ketones. Among various solvents, 2-butanol exhibited the best ability to devulcanize sulfur-cured styrene-butadiene rubber (SBR) rubber. Duration of the process is about 20 minutes.

Reported data on surface devulcanization experiments were obtained by treating small amounts of crumb rubber in the gas chromatography column. The solvent suitable for this process should have a critical temperature in the range of about 200° to 350°C (400° to 650°F). The process produces a slurry of the surface devulcanized crumb rubber that has to be separated from the solvent. In this process, a preferential breakage of S-S and C-S bonds appears to take place, with little breakage of the main chains. The obtained surface modified crumb rubber was subjected to vulcanization as obtained and also in blends with virgin rubber. The vulcanizates exhibited a good retention of mechanical properties in blends with virgin rubber. However, this process has been tested only on a small laboratory scale.

Oils and Chemicals

The De-Link technology for the devulcanization of sulfur-cured scrap elastomers uses 100 parts of 40-mesh or finer crumb mixed with 2 to 6 parts of De-Link reactant in an open two-roll mixing mill (Kohler & O'Neill, 1997; Sekhar & Kormer, 1995). The De-Link reactant, called De-Vulc, is a proprietary material and its nature and composition are not disclosed. No evidence is available to demonstrate that the De-Link process is used beyond laboratory or pilot scale.

Diallyl disulfide is the major constituent in a simple process for reclaiming rubber using a vegetable product that is a renewable resource material (De, et al., 1997; De, et al., 2000; De, et al., 1999). Other constituents of this material are different disulfides, monosulfides, polysulfides, and thiol compounds.

Sulfur vulcanized natural rubber (NR) can be completely recycled at 200° to 225°C (392° to 437°F) by using diphenyldisulphide (Knorr, 1994). A 1999 report (Verbruggen, et al.) listed the efficacies of various disulphides used as recycling agents for NR and ethylene propylene diene monomer rubber (EPDM) vulcanizates. While complete devulcanization was observed on sulfur-cured NR at 200°C (392°F), a decrease on crosslink density by 90 percent was found when EPDM sulfur vulcanizates and diphenyldisulphide were heated to 275°C (527°F) in a closed mold for two hours. At the same time, EPDM cured by peroxide showed a decrease in crosslink density of about 40 percent under the same conditions.

Inorganic Compounds

In addition to the use of organic chemicals, rubbers can be devulcanized by means of inorganic compounds. Discarded tires and tire factory waste have been devulcanized by desulfurization of suspended rubber vulcanizate crumb (10 to 30 mesh) in solvents such as toluene, naphtha, benzene, cyclohexane, etc. in the presence of sodium (Myers, et al., 1997). The alkali metal cleaves mono-, di-, and polysulfidic crosslinks of the swollen and suspended vulcanized crumb rubber at around 300°C (575°F) in the absence of oxygen.

However, this process may not be economical because it involves swelling of the vulcanized crumb rubber in an organic solvent. In this process, the metallic sodium in a molten condition should reach the sulfidic crosslink sites in the crumb rubber. In addition, the solvents may cause pollution and become hazardous. Another proposed method uses an iron oxide phenyl hydrazine-based catalyst to reclaim powder rubbers (Kawabata, et al., 1981) and copper (I) chloride-tributyl amine catalyst (Kawabata, et al., 1979).

The devulcanization process by use of inorganic compounds is suitable for devulcanization of finely ground tire rubber. However, devulcanization is accompanied by a severe breakdown of the rubber chains. So far, the process has been carried out only on a small laboratory scale.

Ultrasonic

Rubber devulcanization by using ultrasonic energy was first discussed in Okuda and Hatano (1987). It was a batch process in which a small piece of vulcanized rubber was devulcanized using 50 kHz ultrasonic waves after treatment for 20 minutes. The process apparently could break down C-S and S-S bonds, but not carbon-carbon (C-C) bonds. The properties of the revulcanized rubber were found to be very similar to those of the original vulcanizates.

One continuous process for devulcanization of rubbers is based on the use of high-power ultrasound electromagnetic radiation. This is a suitable way to recycle waste tires and waste rubbers. The ultrasonic waves, at certain levels, in the presence of pressure and heat, can quickly break up the three-dimensional network in crosslinked, vulcanized rubber. The process of ultrasonic devulcanization is very fast, simple, efficient, and it is free of solvents and chemicals. The rate of devulcanization is approximately one second. This may lead to the preferential breakage of sulfidic crosslinks in vulcanized rubbers. (Isayev, 1993; Yu. Levin, et al., 1996; Isayev, et al., 1997; Yun, et al., 2001; Yun & Isayev, April 2003).

Under a license from the University of Akron for the ultrasonic devulcanization technology, NFM Company of Massillon, Ohio, has built a prototype of the machine for ultrasonic devulcanization of tire and rubber products (Boron, et al., 1996; Boron, et al., 1999). It was reported that retreaded truck tires containing 15 and 30 weight percent (percent by weight) of ultrasonically-devulcanized carbon black-filled SBR had passed the preliminary dynamic endurance test (Boron, et al., 1999).

Extensive studies on the ultrasonic devulcanization of rubbers, and some preliminary studies on ultrasonic decrosslinking of crosslinked plastics, showed that this continuous process allows recycling of various types of rubbers and thermosets (Isayev, 1993; Hong & Isayev, 2002 (pp. 160–168); Shim, et al., 2002; Shim & Isayev, 2003; Gonzalez-de Los Santas, et al., 1999).

As a consequence of the process, ultrasonically-devulcanized rubber becomes soft, therefore enabling this material to be reprocessed, shaped, and revulcanized in very much the same way as virgin rubber. This new technology has been used successfully in the laboratory to devulcanize ground tire rubber (commonly referred to in the industry as GRT) (Isayev, et al., 1995; Yun, et al., 2001; Boron, et al., 1996), unfilled and filled rubbers N (Hong & Isayev, 2001; Yu. Levin, et al., 1996; Isayev, et al., 1997; Diao, et al., 1998; Shim, et al., September 2002; Ghose & Isayev, 2003), guayule rubber (Gonzalez-de Los Santas, et al., 1999), fluoroelastomer, ethylene vinyl acetate foam, and crosslinked polyethylene (Isayev, 1993; Isayev & Chen, 1994). After revulcanization, rubber samples exhibit good mechanical properties, which in some cases are comparable to or exceeding those of virgin vulcanizates.

Structural studies of ultrasonically-treated rubber show that the breakup of chemical crosslinks is accompanied by the partial degradation of the rubber chain; that is, the C-C bonds (Isayev, et al., 1995; Tukachinsky, et al., 1996; Yu. Levin, et al., 1997 (pp. 641–649); Yushanov, et al., 1998). The degree of degradation of C-C bonds can be substantial, depending on conditions. The mechanism of rubber devulcanization under ultrasonic treatment is presently not well understood, unlike the mechanism of the degradation of long-chain polymer in solutions irradiated with ultrasound (Suslick, 1988).

Ultrasonic devulcanization also alters the revulcanization kinetics of rubbers. The revulcanization of devulcanized SBR appeared to be essentially different from those of virgin SBR (Yu. Levin, et

al., 1997, pp. 120–128). The induction period is shorter or absent for revulcanization of devulcanized SBR. This is also true for other unfilled and carbon black-filled rubbers such as ground rubber tire (GRT), SBR, natural rubber (NR), ethylene propylene diene monomer (EPDM), and butadiene rubber (BR) cured by sulfur-containing curative systems, but not for silicone rubber cured by peroxide.

Ultrasonically-devulcanized rubbers consist of sol and gel. The gel portion is typically soft and has significantly lower crosslink density than that of the original vulcanizate. Due to the presence of sol and soft gel, the devulcanized rubber can flow and is subject to shaping. Crosslink density and gel fraction of ultrasonically-devulcanized rubbers were found to correlate by a universal master curve (Yushanov, et al., 1996; Diao, et al., 1999; Yushanov, et al., 1998). This curve is unique for every elastomer due to its unique chemical structure.

Microwave

Microwave technology has also been proposed to devulcanize waste rubber (Fix, 1980; Novotny, et al., 1978). This process applies the heat very quickly and uniformly on the waste rubber. The method employs the application of a controlled amount of microwave energy to devulcanize a sulfur-vulcanized elastomer—containing polar groups or components—to a state in which it could be compounded and revulcanized into useful products such as hoses.

The process requires extraordinary or substantial physical properties. On the basis of the relative bond energies of C-C, C-S, and S-S bonds, the scission of the S-S and carbon-sulfur crosslinks appeared to take place. However, the material to be used in the microwave process must be polar enough to accept energy at a rate sufficient to generate the heat necessary for devulcanization. This method is a batch process and requires expensive equipment.

Recently, thermogravimetry was employed to study the changes occurring in rubber vulcanizates during devulcanization. These were carried out by microwave treatment (Kleps, et al., 2000). This study determined the degree of degradation of the polymer chains in response to microwave treatment. It also established the conditions of devulcanization needed to obtain the best properties of rubber devulcanizates for reuse in rubber processing.

Biological

Biological processing of vulcanized rubber has been used in some cases, although vulcanized materials are resistant to normal microbial attack (Adhikari, et al., 2000). Several researchers have reported using different types of microorganisms to attack the sulfur bonds in vulcanized elastomers. One process uses a chemolithiotrope bacterium in a liquid solution to depolymerize the surface of powdered elastomers. The polymer chains then are available to bond again during the vulcanization process. The same type of bacterium has been shown to devulcanize crumbed scrap rubber when held in an aerated liquid suspension of microorganisms (Straube, et al., 1994).

Reportedly, sulfur can be recovered in this process, as well as devulcanized rubber. Loffler and colleagues studied the devulcanization of high-quality rubber products by different species of *Thiobacillus* in 1993. The rate of devulcanization was found to be a function of particle size, with best results secured for particles in the range of 100 to 200 microns. However, only a small percentage of the sulfur links were broken after 40 days of exposure.

In 2003, Bredberg investigated and reported on the ability of sulfur-oxidizing bacteria *Acidithiobacillus* and sulfur-reducing *P. furiosus* to break sulfur crosslinks in vulcanized rubber materials. The report covered the effect of grinding methods on reaction rates. Apparently, these types of biological devulcanization processes are exclusively or primarily limited to the surface

layers of the elastomers (Christiansson, et al., 1998). This circumstance may explain the overall low rates of desulfurization based on total mass processed.

Several researchers have reported on devulcanization of vulcanized cis-1,4-polyisoprene, a primary constituent of natural rubber (Tsuchii, et al., 1985; Tsuchii, et al., 1997; Tsuchii & Takeda, 1990). This process employed a bacterium of the species *Nacardia*, and a white rot fungus, *C. subvermispra* (Sato, et al., 2003). Holst, et al. in 1998 gives nine other groups or mixtures of microorganisms that have been used for desulfurization of GRT or constituents thereof.

Naturally occurring microorganisms are susceptible to the environmental conditions within the processing system. Thus, toxicity to chemical compounds in the substrate (that is, waste tire rubber) is an overriding concern. Maintenance of proper environmental conditions (availability of nutrients, operating temperature, etc.) during processing is another concern. In fact, methods of determining and preventing biodegradation of rubber have been investigated extensively (Cundell & Mulcock, 1973; Cundell, et al., 1973; Keursten & Groenevelt, 1996; Williams, 1986). Some effort has been expended on isolating and enriching microbial cultures for devulcanizing NR and SBR using biotechnology. Other studies focused on controlling the microbial toxicity of rubber constituents (Bredberg, 2003; Bredberg, et al., 2002).

Other

Mechanical

A mechanical or reclaimator process has been used for the continuous reclaiming of whole tire scrap (LaGrone, 1986; Szilard, 1973; Bryson, 1979; Klingensmith, 1991; Leyden, 1991). Fine rubber crumb (typically, 30 mesh), mixed with various reclaiming oils, is subjected to high temperature with intense mechanical working in a modified extruder for reclaiming the rubber scrap.

Steam With or Without Chemicals (Digester)

The digester process uses a steam vessel equipped with a paddle agitator for continuous stirring of the crumb rubber while steam is being applied (Makarov & Drozdovski, 1991; Warner, 1994; Klingensmith & Baranwal, 1998; LaGrone, 1986; Bowers, et al., 1986; Knorr, 1995; Schaefer, 1986; Schaefer & Berneking, 1986; Szilard, 1973).

The wet process may use caustic and water mixed with the crumb rubber, while the dry process uses steam only. If necessary, various reclaiming oils may be added to the mixer in the vessel. The dry digester has the advantage of less pollution being generated. Scrap rubber containing natural and synthetic rubbers can be reclaimed by the digester process, with the use of reclaiming oil having molecular weights between 200 and 1,000. These consist of benzene, alkyl benzene, and alkylate indanes. The composition of this reclaiming oil and the improved digester process using such reclaiming oil have been patented (Bryson, 1979).

Biological and Microwave

Both microbial oxidation and microwave energy have been employed in a two-stage system developed and patented by the Westinghouse Savannah River Company, LLC, for the purpose of devulcanizing waste tire rubber (Fliermans & Wicks, 2000). The process has developed only to the point of proving conceptual feasibility based on limited testing (Westinghouse Savannah River Company, 2004).

Technology Researchers and Providers

In preparing the literature review and consulting other sources, CalRecovery identified a number of entrepreneurial groups and technology suppliers that have developed (or attempted to develop) and/or researched devulcanization processes. These are listed in Table 1. As far as could be determined from the available information, all of the processes listed in Table 1 are at the research or developmental level. None are applied to devulcanizing waste tires on a continuous commercial basis.

The history of rubber devulcanization is checkered with research on various types of technologies. Certain technologies have been discontinued for a variety of reasons, and some researchers have maintained secrecy about their findings. Numerous licensing agreements are in existence. Thus, the listing given in Table 1 likely contains not only the names of the primary technology developers, but also those that license the technologies for use as is or with some type of modification. In many cases, CalRecovery found it difficult to identify or determine the developer of the technology, as opposed to those marketing or licensing the technologies.

As shown in Table 1, CalRecovery identified technologies with apparent origins in North America, including three in California, and in several other countries.

Table 1. Identified Devulcanization Technologies

Company	Location	Process
American Rubber Technologies, Inc.	Florida	Chemical/Mechanical
BF Goodrich Company	Akron, Ohio	Chemical/Mechanical
Exxon	USA	Chemical/Mechanical
Goodyear Tire & Rubber Company	Akron, Ohio	Microwave
Goodyear Tire & Rubber Company	Akron, Ohio	Chemical/Thermal
Guangzhou Research Institute	Guangzhou, China	Chemical/Mechanical
LandStar Rubber, Inc.	Scottsdale, Ariz.	Proprietary license
Levgum, Ltd.	Israel	Chemical/Mechanical
Ultramer/National Feedscrew & Machining, Inc.	Massillon, Ohio	Ultrasonic/Mechanical
NRI Industries	Toronto, Ont., Canada	Mechanical
Pacific Northwest National Laboratory (RubberCycle)	Richland, Wash.	Biological
POLYMERight, Inc.	Fremont, Calif.	Chemical/Mechanical
Quantum Polymer	Cleveland, Ohio	Chemical
Redwood Rubber, LLC	Corte Madera, Calif.	Ultrasonic
Revulcon	Germany	Mechanical
Rubberworks International	New York	Ultrasonic/Mechanical
Santee River Rubber Company	South Carolina	Mechanical/unknown
SoftStone	Pottsboro, Tex.	Same as Levgum
STI-K Polymers America, Inc. (De-Link/-Vulc)	unknown	Mechanical/Chemical
Sumitomo Rubber Industries, Ltd.	Kobe, Japan	Biological
Tires2Oil	Irvine, Calif.	Chemical
Toyoda Gosei	Japan	Mechanical
TRC Industries	Stow, Ohio	Steam/Mechanical

Company	Location	Process
Tyre-Plex	Downingtown, Penn.	Pulverization
University of Akron	Akron, Ohio	Ultrasonic
Watson Brown HSM, Ltd.	Glossop, England	Mechanical
Westinghouse Savannah River Company	Aiken, S.C.	Biological/Microwave

Chapter 3. Technology Descriptions and Analysis

Introduction

As described in Chapter 2, several types of devulcanization technologies have been applied to the devulcanization of waste tire rubber. Other technologies may have the capacity for devulcanization based on processing of other rubber or thermoplastic feedstocks. Various types of these technologies are described in this chapter, including performance of devulcanized materials or mixtures where such data could be found.

Methodology

Information for this task was primarily secured using the following resources:

- Popular and peer-reviewed literature.

- Waste tire processing equipment manufacturers.

- Websites of devulcanization entrepreneurs and other sources of devulcanization technologies.

- Telephone calls and e-mail communications to researchers and technology vendors.

Despite a concerted effort to collect detailed data and information on the various types of devulcanization technologies, only limited information was found to be in the public domain or of a non-proprietary nature. Consequently CalRecovery, in a number of cases, synthesized general technology descriptions based on the best non-proprietary data that was available and on its engineering judgment.

Few lab-scale or commercial-scale devulcanization systems exist in the United States. Test or performance data released in the public domain is limited, and researchers maintain tight-fisted control of data to protect actual or perceived technical know-how and competitive advantage. In most cases where reports of data and information on devulcanization appear in the available literature, conditions (feedstock characteristics, operating, analytical, etc.) are insufficiently described. These circumstances limited CalRecovery's attempts to interpret the data and technologies in the current study.

Devulcanization Systems

The process of devulcanizing waste rubber can be broken down into two separate sequential and integrated steps. The first (or pre-processing) step is size reduction. The waste is reduced in size so that it can be fed into the system that actually performs most if not all of the chemical bond-breaking. The second step is the devulcanization process, or the breaking of the chemical bonds (primarily the sulfur bonds). The output product from the process is devulcanized rubber.

Devulcanization system suppliers may supply only the devulcanization process itself, or in combination with a size reduction process.

Pre-Processing of Feedstock (Step 1)

Regardless of the specific type of devulcanization technology (biological, ultrasonic, etc.), devulcanization systems in general are composed of several subsystems. Common to essentially all devulcanization technologies is the need for a finely sized, vulcanized rubber feedstock. This is because the chemical, thermal, or biological conversion subsystems accept only finely sized

feedstock for devulcanization. Also, finely sized feedstock creates substantial surface area for devulcanization reactions to take place.

Consequently, the developers of devulcanization technologies either assume that their operation will procure appropriately sized feedstock from a third party or they must include size reduction equipment as part of their overall devulcanization system. Very generally, a typically desired particle size of feedstock for the devulcanization process is on the order of 10 to 30 mesh. However, there are exceptions to this generality, as discussed later.

There are three primary commercial methods of grinding waste rubber:

1. Ambient grinding.

2. Cryogenic grinding.

3. Wet-ambient grinding.

Generally, several stages of size reduction are used to prepare waste tires or vulcanized scrap rubber for devulcanization. The first stage of size reduction typically reduces the rubber feedstock to a nominal 1- to 2-inch particle size. When processing waste tires, a magnetic separator and a fiber separator are subsequently used to remove the steel and fiber constituents (contamination). The resulting clean, primary-grind product is then further reduced in size using an ambient ground mill, or ground into fine particles while frozen using cryogenic grinding.

One method for producing fine-mesh rubber is cooling scrap tires in liquid nitrogen, and then pulverizing the brittle material in a high-speed hammermill. The ground rubber has a fine particle size, in the range of 30 to 100 mesh.

Another method of producing finely sized rubber is ambient mechanical size reduction using a high-powered rubber mill set at close nip. This method produces 10- to 30-mesh material. Multiple grinder passes can be used to further reduce the particle size.

Lastly, wet or solution process grinding can be used to produce rubber particle size distributions in the range of 200 to 500 mesh.

Grinding processes for tire rubber are well developed. They are widely used for recycling of tire rubbers and rubber wastes. Also, industrial machines are available for breakup and separation of rubber from steel, cord, and fabrics that are present in tires. High industrial rates for production of tire rubber crumbs have been achieved. With waste tire size reduction comes high energy requirements. This is a significant issue if finely-sized rubber feedstock is needed, as is diminution of rubber properties due to heat generation during size reduction.

Devulcanization Processes (Step 2)

The following devulcanization processes are described in this chapter:

- Chemical.

- Ultrasonic.

- Microwave.

- Biological.

- Other.

Chemical

Chemical agents have been used to devulcanize scrap rubber since the 1960s. Early research was performed by the Malaysian Rubber Producers Research Association (MRPRA) (Warner, 1994). Initial studies performed by Saville and Watson (Warner, 1994) on low molecular mass compounds paved the way for later researchers to investigate the action of chemical probes. Further studies have been carried out to ascertain which bonds, specifically, were being cleaved by the chemical processes.

Most chemical devulcanization processes are batch processes that involve mixing size-reduced rubber particles and chemical reactants in a temperature- and pressure-controlled mixer. Generally speaking, rubber is fed into a mixer with a devulcanizing agent and heated. In the case of abandoned technology of the mid-1990s (namely, the De-Link Recycling System promoted by STI-K Polymers), the recommended ratio of chemical agent to a finely sized (for example, 40 mesh) rubber feedstock was approximately 2 to 6 parts by weight chemical to 100 parts rubber (Kohler & O'Neill, 1997; Sekhar & Kormer, 1995; Findians Oy, 2003). Once the design reaction time has elapsed, the contents are then rinsed, filtered, and dried to remove any remaining unwanted chemical components. The product can then be bagged or otherwise processed for resale. A flow diagram of the process is given in Figure A.

Figure A. Schematic Diagram of a Chemical Devulcanization System
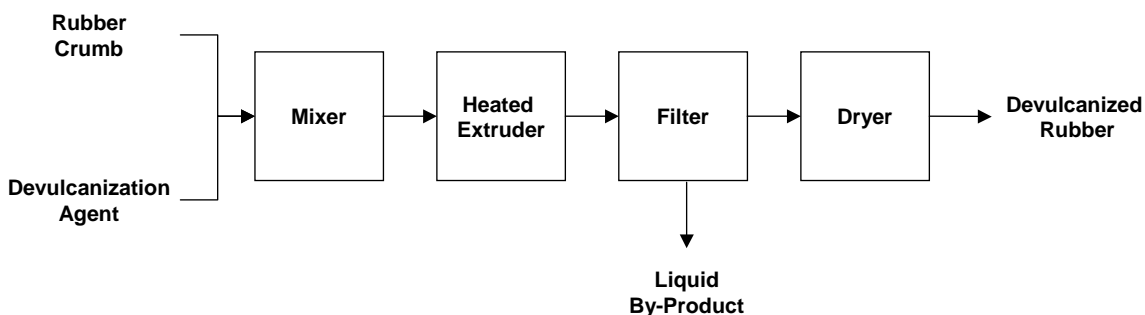
Various chemical agents have been used in the chemical devulcanization processes developed over the years. The agents include petroleum-based solvents (for example, toluene), thiol-amine reagents, hydroxide, disulfide compounds, or chlorinated hydrocarbons. With some chemical agents, a catalyst is also used to promote the desired reactions.

The following two chemical devulcanization processes are indicative of the current commercialization efforts, lab-scale systems, or both.

POLYMERight, Inc., a California-based company, is developing a rubber reclaiming process where a measured amount of proprietary devulcanization chemical agent (DB-26) is added to a mixer and heated with a corresponding amount of vulcanized rubber. After the requisite exposure time is elapsed, the slurry is forced through an extruder at temperatures between 500° and 600°F (260° and 315°C). Once cooled, the now devulcanized rubber is ready for sale. According to company information, POLYMERight's technology has been demonstrated on a laboratory scale (10 to 15 lb/hr), but it has yet to be demonstrated on a commercial scale.

Another company marketing a chemical devulcanization technology is Tires2Oil, Inc. (T2O). The T2O process takes place in a mixer or reactor. In the case of tire rubber, granulated rubber (approximately 30 mesh) is separated from the fiber and metal fractions and loaded into a reactor.

The rubber is then mixed with a proprietary solvent and treated at thermodynamically critical conditions of temperature and pressure.

When the requisite reaction time has elapsed, the mixture is cooled and the gases vented and stored. The oil and solvent fraction is drained from the reactor, and the carbon black is removed for additional processing. The solvent is then separated by distillation—or other means—for reuse. The sulfur, which has been collected from the mixture and scrubbed from the gases, reportedly can also be sold. Carbon black recovered from the process can also be further processed by T2O for resale. T2O also claims to have developed additional processes that are capable of recovering the other chemical constituents of vulcanized rubber; for example, oils, solvents, and sulfur (Tires2Oil, 2004).

Ultrasonic

Most companies marketing ultrasonic devulcanization technologies are utilizing very similar technologies involving cold feed extruders and varying physical arrangements of ultrasonic equipment. The recent technologies are continuous processes, as opposed to batch.

Ultrasonic devulcanization technology is actually composed of a "devulcanization system"—namely, extrusion and ultrasonic processing. Many of the designs are similar. Two key differences in some cases are the equipment and materials used to generate the ultrasonic energy required for the process, and the positioning of the transducer(s) relative to the extruder.

Two different arrangements of ultrasonic devulcanization systems are shown in Figures B and C. In this type of devulcanization system, size-reduced rubber particles are loaded into a hopper and are subsequently fed into an extruder. The extruder mechanically pushes and pulls the rubber. This mechanical action serves to heat the rubber particles and softens the rubber. As the softened rubber is transported through the extruder cavity, the rubber is exposed to ultrasonic energy.

The resulting combination of heat, pressure, and mechanical mastication is sufficient to achieve varying degrees of devulcanization. The time constant of the devulcanization process takes place in seconds. Essentially all of the rubber entering the process is discharged from the extruder in semi-solid product stream. Process losses would be primarily those due to emissions of fine particulates or of gases, if any, generated due to the mechanical and thermal processes occurring during the devulcanization process. After exiting through the extruder die, the rubber is passed through a cooling bath and then dried.

Figure B. Schematic Diagram of an Ultrasonic Devulcanization System Showing a Mid-Extruder Location for the Ultrasonic Subsystem
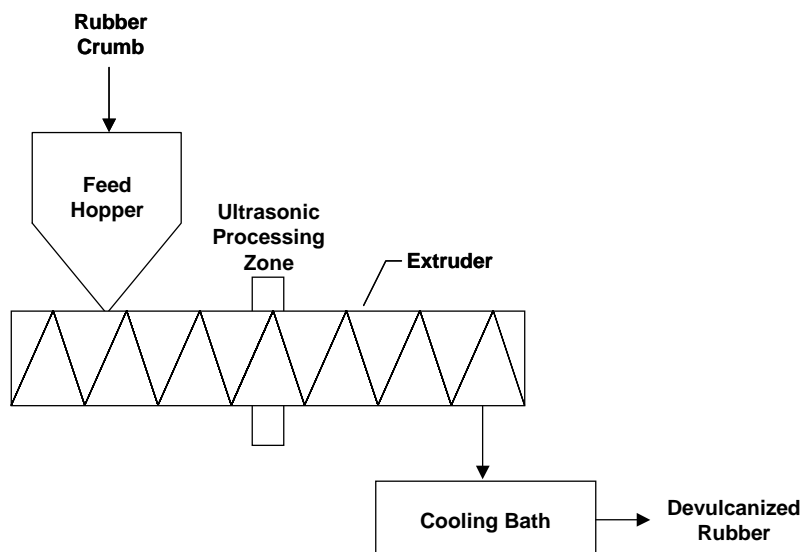
Figure C. Schematic Diagram of an Ultrasonic Devulcanization System Showing the Ultrasonic Subsystem Located at the Discharge End of the Extruder
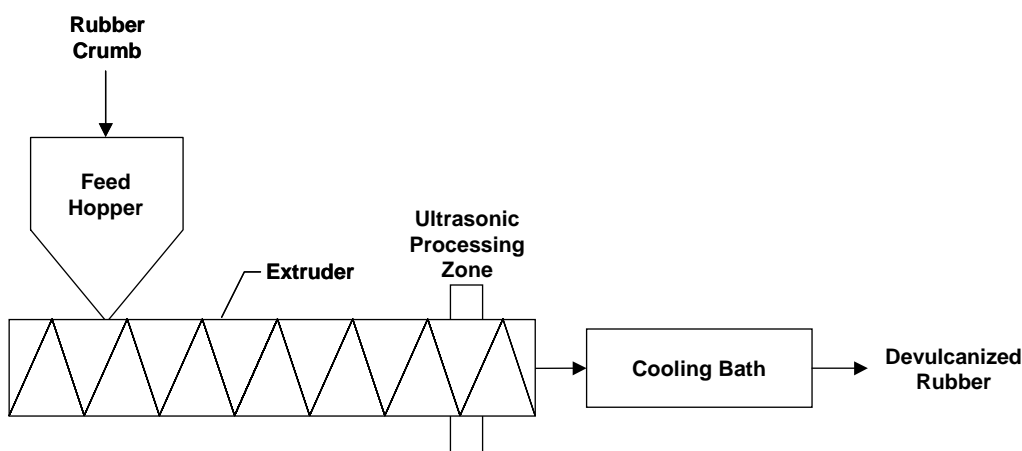
In terms of laboratory or commercial ultrasonic processing systems that are operational or were in the last five to eight years, the following descriptions are representative examples.

The University of Akron has a laboratory-scale ultrasonic devulcanization system that utilizes mechanical extrusion and ultrasonic energy to devulcanize scrap rubber. The extruder reportedly has a capacity of approximately 50 lb/hr (Isayev, 1993; Isayev & Chen, 1994; Isayev, et al., 1995; Tukachinsky, et al., 1996; Yun, et al., 2001). The required particle size of the scrap rubber feedstock is generally 10 to 30 mesh. Processing rates during laboratory test runs of about 5 lb/hr have been reported when processing tire rubber (Hong and Isayev, 2002, pp. 160–168). At these processing rates, the system requires approximately 1 to 1.5 kW ultrasonic energy (20 kHz) source.

Under a license from the University of Akron's ultrasonic devulcanization technology, Ultramer, Inc., of Massillon, Ohio, has reportedly built a prototype machine for ultrasonic devulcanization of tire and rubber products. The project manufactured retreaded truck tires containing 15 and 30 weight percent of ultrasonically devulcanized carbon black-filled SBR.

Also, Redwood Lumber, LLC, Corte Madera, Calif., has reportedly constructed and operated a proprietary ultrasonic devulcanization system. The process is based on the use of "magnetostriction-based" ultrasound (Ruhman, et al., 2000). The processing capacity is low but unknown as of this writing.

Microwave

Microwave technology has also been proposed to devulcanize waste rubber. This process applies the heat energy very quickly and uniformly on the waste rubber. However, any vulcanized rubber used in the microwave process must be sufficiently polar in structure so that the microwave energy can be absorbed at a rate adequate to generate the heat necessary for devulcanization. This method is a batch process; a schematic diagram of the general process flow is shown in Figure D. Microwave energy requirements are in the range of .041 and 0.177 kW/lb in the case of devulcanizing EPDM using microwave frequencies between 915 and 2450 MHz. Processing times are approximately five minutes, with 90 to 95 percent recovery of rubber (Adhikari, et al., 2000).

Figure D. Schematic Diagram of a Microwave Devulcanization System
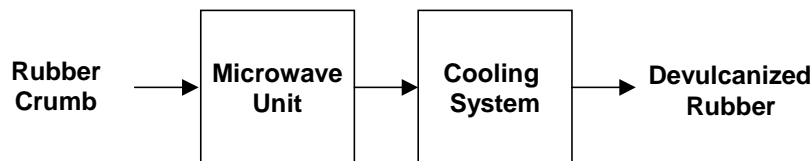
The only rubber used in tires that is sufficiently polar to be effectively devulcanized by microwave energy is EPDM. This represents a small fraction of the rubber used in tires, probably well under 5 percent, because it is primarily used in whitewalls and raised white letters. Most types of rubber used in tire manufacture (natural rubber/polyisoprene, styrene-butadiene rubber, polybutadiene, polyisobutylene) are not sufficiently polar to be devulcanized by microwave technology because sufficient heating of the rubber constituents cannot be obtained to promote devulcanization.

The only reasonable use for microwave devulcanization is on compounds containing primarily a polar rubber, such as EPDM hose. Goodyear obtained a U.S. patent for the use of microwave energy to devulcanized rubber in 1978 (Novotny, et al., 1978). The process was used to devulcanize EPDM hose scrap for some years, then was abandoned due to unfavorable economics (Klingensmith, 1996).

Biological

The concept of utilizing bacteria to devulcanize scrap rubber has been investigated for at least 30 years. For example, Beckman, Crane, Kay, and Laman concluded an in-depth evaluation of the biodegradation of rubber in 1974 (Warner, 1994). Although vulcanized materials are resistant to normal microbial attack and compounded rubber can act as a biocide, several researchers have reported using different types of microorganisms to attack the sulfur bonds in vulcanized elastomers.

Bacterial devulcanization is performed by mixing finely ground rubber with media containing the appropriate bacterium in a temperature-controlled bioreactor. The slurry is then maintained at a prescribed temperature and pressure for the duration of the treatment. Biological contact time is approximately ten to a few hundred days. Solids content of the slurries used in research are approximately 5 percent by weight (Holst, et al., 1998; Christiansson, et al., 1998).

Once processed, the newly devulcanized material is rinsed and filtered to remove the microorganisms, then dried for sale. An important fact of note is that this technology requires an extremely fine feedstock in order to achieve useful degrees of devulcanization [for example, 200 mesh (75 microns) (Romine, 1997) or 100 to 200 microns (Loffler et al., 1993)]. A generic processing diagram for a biological devulcanization system is shown in Figure E.

Figure E. Schematic Diagram of Biological Devulcanization System
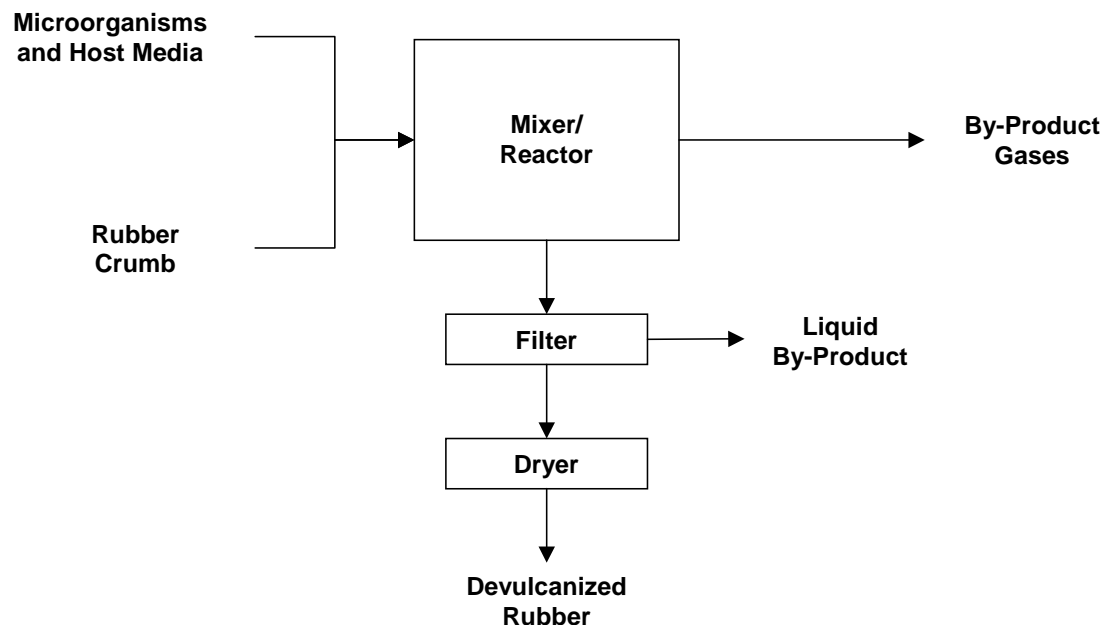
Other

Mechanical

Mechanical devulcanization is achieved through the repeated deformation of rubber particles under specific conditions of temperature and pressure.

One mechanical process implemented by Toyoda Gosei (TG) utilizes a "modular screw-type reactor" to manipulate and stress the rubber until it is plasticized and then ultimately devulcanized (Fukumori et al., 2002). By manipulating screw configuration and rotational speed, and processing temperature, researchers are able to control the duration of the treatment. In this way they can, to some extent, control the properties of the devulcanizate.

The TG process can accept and process rubber feedstock up to about 5 to 10 mm. According to the developers, the process requires about 100 Kw (kilowatts) to process 200 to 300 kg (kilograms)/hr of rubber, or approximately 0.4 kW/kg. The TG process has been primarily, if not exclusively, used to devulcanize specific types of rubber compounds, such as NR and SBR.

Steam With or Without Chemicals (Digester)

Steam devulcanization of crumb rubber uses a steam vessel equipped with an agitator for continuous stirring of the crumb rubber while steam is being applied. There are two variants of the basis steam process, namely, "wet" and "dry." The wet process uses caustic and water mixed with the rubber crumb, while the dry process uses only steam.

If necessary, various reclaiming oils may be added to the mixture in the reaction vessel. In one case, a wet process using diaryl disulfide and reclaiming oils with saturated steam at 190°C (374°F) was fed finely ground NR and synthetic rubber scraps. A charge of about 440 lbs. was partially devulcanized after 15 to 17 hours of processing. This process required 12 hours at ambient temperature for pre-treatment and 3 to 5 hours for steam or high temperature treatment (Adhikari, et al., 2000).

The dry process digester has the advantage of generating less pollution than the wet process. Scrap rubber containing natural and synthetic rubbers can be reclaimed by the steam digestion process. Reclaiming oil used for this process has molecular weights between 200 and 1000, consisting of benzene, alkyl benzene, and alkylate indanes. A generic processing diagram for steam devulcanization is shown in Figure F.

Figure F. Schematic Diagram of a Steam Devulcanization System
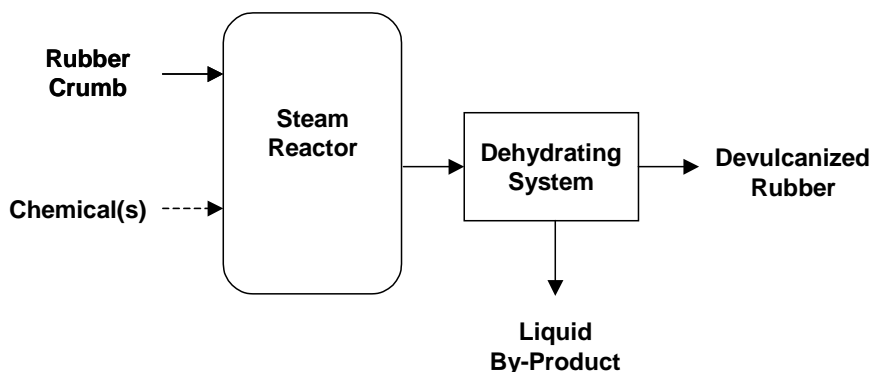
Product Characteristics

Processing Parameters and Compound Properties

Background

The properties of devulcanized rubber, and properties of materials manufactured from this substance, depend on the results of the devulcanization process. These properties also depend on the other constituents of the product that incorporates the devulcanized rubber. In the industry, the formulation process is referred to as compounding.

Compounding is important in determining the characteristics of products manufactured with devulcanized rubber. Therefore, we include a section on compounding and its influence on material properties as an introduction to the discussion of devulcanized product characteristics. The discussion also serves as a backdrop to the assessment presented in Chapter 5, Market Analysis.

Compounding

Compounding is the process of combining rubber with all of the ingredients that will be present in the final vulcanized product. A compound is the recipe that is mixed and milled, then extruded, calendered, or molded into the desired shape, and cured at high temperature. This recipe would include the carbon black and/or other fillers, extender oil, antioxidants, antiozonants, sulfur, and other curatives, such as accelerators and activators.

The term "compound" typically refers to rubber that has been pre-mixed and milled to be shaped and cured into a finished product. For example, "custom compounders" produce compound and sell it to manufacturers of finished rubber goods. A tire retreader would buy "tread compound" already extruded into the approximate shape of a tread, apply it to a tire carcass, and then vulcanize it in a mold. The term is also used to refer to a cured compound. For example, all of the properties in the examples given below are properties of the cured compounds.

The compounding of rubber is a synthesis of art and science. While much has been learned and published about rubber compounding, the practice still involves both intuition and trial-and-error. General principles provide at least a good starting point for compound development. For example, carbon black is a "reinforcing" filler. Carbon black increases the tensile strength of rubber up to a point, usually to the loading level of approximately 50 parts per hundred (phr). With most mineral fillers, tensile strength drops as the level of filler is increased.

The following examples of compound properties for different applications give some specifics as to how compound properties vary with the amounts of fillers and oils used (*Vanderbilt Rubber Handbook*, R.T. Vanderbilt Company, 1990). This standard reference has dozens of typical rubber compounds for many different applications, some of which could be used as the basis for test compounds using devulcanized rubber.

Examples

The loading of carbon black and minerals affects properties of natural rubber. As indicated in Tables 2 and 3, values of hardness and modulus increase as loading levels increase, while elongation and tensile strength decrease. Tensile strength begins to drop off when carbon black loadings exceed the 50 parts per hundred (phr) range. This is why most high-strength applications use this range of carbon black loading.

Table 2. Effect of Black Loading Materials in Natural Rubber

Constituent and Loading	300% Mod, MPa (psi)	Tensile MPa (psi)	Elong. (%)	Hard. (Shore A)	Tear, kN/m (pli)	Compr. Set (%)	Mooney (t5/ML)
Thermax (MT) N-990							
25 phr	2.8 (400)	22.1 (3200)	660	43	28.2 (160)	13	14/11
50 phr	4.4 (640)	21.4 (3100)	620	49	45.8 (260)	15	11/13
75 phr	6.3 (920)	18.8 (2730)	600	55	42.2 (240)	14	9/17
100 phr	8.5 (1230)	15.3 (2200)	530	80	44.9 (255)	15	9/17
125 phr	10.3 (1500)	11.6 (1580)	430	87	35.2 (200)	15	7/18
GPF N-660							
25 phr	4.6 (680)	25 (3620)	630	48	59.9 (340)	11	12/16
50 phr	9.3 (1350)	23.2 (3370)	540	57	66.0 (375)	15	10/27
75 phr	15.0 (2170)	25.1 (3040)	440	68	52.8 (300)	16	8/36
100 phr	--	18.4 (2670)	280	76	22.9 (130)	15	6/48
HAF N-330							
25 phr	5.1 (740)	27.6 (4000)	640	51	92.4 (525)	12	10/22
50 phr	11.9 (1720)	28.5 (4130)	570	64	101.2 (575)	15	8/39
75 phr	21.2 (3070)	24.7 (3580)	400	74	73.9 (420)	16	6/62

Base Compound:
SMR-5

Vanplast R
Stearic Acid
Zinc Oxide
Agerite Stalite S
Sulfur
Altax
Methyl Tuads

All compounds cured 10 minutes at 153°C (307°F).
Tear measured on Die A samples.
Compression set measured after 22 hours at 70°C (158°F).
Mooney measured at 132°C (270°F).
Source: R.T. Vanderbilt Company, 1990.

Table 3. Effect of Mineral Loading Materials in Natural Rubber

Constituent and Loading	300% Mod., MPa (psi)	Tensile MPa (psi)	Elong. (%)	Hard. (Shore A)	Tear, kN/m (pli)	Compr. Set (%)	Mooney (t5/ML)
Calcium Carbonate (ground)							
50 phr	2.1 (300)	17.8 (2580)	700	44	10.6 (60)	17	17/12
75 phr	2.3 (340)	16.6 (2400)	680	47	14.0 (80)	18	17/13
100 phr	2.8 (370)	14.4 (2090)	640	51	13.2 (75)	19	16/17
150 phr	2.5 (360)	10.8 (1560)	620	56	13.2 (75)	22	13/20
DIXIE CLAY							
50 phr	5.0 (730)	21.9 (3170)	860	45	14.0 (80)	37	25/16
75 phr	6.8 (960)	19.1 (2770)	570	46	14.0 (80)	45	24/21
100 phr	9.1 (1170)	20.0 (2900)	530	53	15.8 (90)	48	18/26
150 phr	11.7 (1700)	16.0 (2320)	400	62	19.4 (110)	52	9/34
Hi-Sil 233							
25 phr	1.9 (270)	20.8 (3010)	760	40	35.2 (200)	27	16/20
50 phr	1.9 (280)	20.0 (2800)	790	50	81.8 (465)	34	15/26
75 phr	3.1 (450)	17.8 (2580)	880	65	40.5 (230)	44	15/78

Base Compound:
SMR-5
Vanplast R
Stearic Acid
Zinc Oxide
Agerite Stalite S
Sulfur
Altax
Methyl Tuads

All compounds cured 15 minutes at 153°C (307°F).
Tear measured on Die A samples.
Compression set measured after 22 hours at 70°C (158°F).
Mooney measured at 132°C (270°F).
Source: R.T. Vanderbilt Company, 1990.

Higher quality compounds of rubber use lower levels of carbon black and mineral loading. Therefore, these compounds possess higher proportions of rubber, as shown by way of examples for SBR compounds in Tables 4A and 4B. As indicated by the data in Tables 4C and 4D, respectively, the automotive mat compound has about six times as much filler (325 phr) as the high-quality shoe sole compound (50 phr).

Table 4A. Properties of Some Compounds Used to Manufacture High-Quality Conveyor Belt Cover (phr)

Constituent	Mix 1	Mix 2
SBR extended with aromatic oil	137.5	--
SBR extended with carbon black	--	162.5
Zinc oxide	4	4
Stearic acid	2	1
Antioxidant	2	2
Sulfur	1.8	1.8
Vanax NS accelerator	1.5	1.5
Methyl Tuads accelerator	0.4	--
Carbon black	70	--
Aromatic oil	10	--

Source: R.T. Vanderbilt Company, 1990.

Table 4B. Properties of Some Compounds Used to Manufacture Medium-Quality Conveyor Belt Cover (phr)

Constituent	Mix 1	Mix 2
SBR extended with aromatic oil	137.5	--
SBR extended with oil and carbon black	--	245
Carbon black	100	
Aromatic oil	40	--
Zinc oxide	4	--
Stearic acid	2	2
Agerite Superflex antioxidant	1	1
Antozite 67P antiozonant	1	1
Sulfur	2	2
Vanax NS accelerator	1.6	1.6
Methyl Tuads accelerator	0.6	0.6

Source: R.T. Vanderbilt Company, 1990.

Table 4C. Properties of Some Compounds Used to Manufacture Automotive Mat (phr)

Constituent	phr
SBR extended with naphithenic oil	150
Zinc oxide	4
Stearic acid	4
Agerite Superflex antioxidant	1.5
Vanwax NS special protective wax	3
Glycol activator	2
Clay, calcium carbonate, silica fillers	325
Naphithenic plasticizer	30
Amax accelerator	2
Methyl Tuads accelerator	0.4
Sulfur	4

Source: R.T. Vanderbilt Company, 1990.

Table 4D. Properties of Some Compounds Used to Manufacture Shoe Sole (phr)

Constituent	High-Quality	Medium-Quality
SBR (45-55 ML4)	100	100
Naphithenic oil	5	5
Zinc oxide	4	4
Stearic acid	2	2
Vanox MBPC antioxidant	1	1
Altax accelerator	1.5	2
Unads accelerator	0.5	0.5
Glycol activator	2	2
Sulfur	2	2.5
Silica filler	50	40
Pliolite S6-B high-styrene resin	--	25
Dixie clay	--	120

Source: R.T. Vanderbilt Company, 1990.

Properties of natural rubber compounds for two different applications are shown in Tables 5 and 6. The radial truck tread described in Table 5 has about half the fillers of the first extrusion compound (AA 515), described in Table 6, and nearly twice the tensile strength. Note also that the second extrusion compound (AA 725) described in Table 6 shows a considerable increase in strength and modulus with the use of more carbon black in place of the clay. This is a good illustration of the reinforcing effect of carbon black, compared with that obtainable with non-reinforcing clay.

Finally, the characteristics of two EPDM hose compounds are presented in Table 7 in order to show one of the most extreme examples of loading levels and their influence in rubber manufacturing. The "highly extended" EDPM hose compound described in the table has 600 phr oil and filler, or about 11 times as much oil and filler as the "steam hose" compound (55 phr), and less than half the strength (6.4 vs. 13.0 MPa) and modulus (2.2 vs. 4.9 MPa). This example shows how much rubber can be saved when property requirements are not critical for product end uses.

Table 5. Characteristics of Radial and Bias Truck Tread Recipes

Ingredients	Radial	Bias
TSR 20 natural rubber	100	--
Budene 1207	--	50
Plioflex 1712	--	68.75
SAF black (N-110)	50	55
Antozite 67P	2	2
Agerite Resin D	2	1.5
Vanax H Special	1.5	3
Aromatic oil	4	12.5
Stearic acid	2	2
Zinc oxide	4	3.3
Sulfur	1.75	1.55
Durax	1.75	--
Vantard PVI	0.5	--
Morfax	--	1
Methyl Tuads	--	0.15
Totals	*169.50*	*200.75*
Rheometer at 150°C (300°F)		
ts_1 (minutes)	7.4	12.2
tc_{90} (minutes)	12.0	36.8
Physical Properties Cured 22 minutes at 150°C (300°F)		
Stress at 300%, MPa (psi)	12.3 (1790)	11.8 (1710)
Tensile strength, MPa (psi)	27.1 (3920)	17.6 (2550)
Elongation at break (%)	550	415
Rebound[a] at 22°C (72°F) (%)	81.9	70

[a] ASTM D1054, cured 32 minutes at 150°C (300°F).
Source: R.T. Vanderbilt Company, 1990.

Table 6. Characteristics of Two NR Extrusion Compounds

ASTM D 2000	AA 515	AA 725
SMR-5	100	100
Stearic acid	0.5	0.5
Zinc oxide	5	5
Agerite Stalite S	2	2
Vanfre AP-2	2	2
Vanplast R	5	5
Circo light oil	8	--
Neophax A	30	15
FEF black (N-550)	30	80
McNamee Clay	40	--
Sulfur	2.75	2.75
Amax	1	1
Methyl Tuads	0.2	0.2
Cured 10 minutes at 153°C (307°F)		
300% modulus, MPa (psi)	5.4 (780)	16.6 (2400)
Tensile strength, MPa (psi)	13.8 (2000)	18.8 (2730)
Elongation (%)	570	370
Hardness (Shore A)	50	68
Tear die A, kN/m (pli)	21.1 (120)	28.2 (160)
Cured 5 minutes at 160°C (320°F)		
300% modulus, MPa (psi)	5.4 (790)	16.1 (2340)
Tensile strength, MPa (psi)	14.5 (2110)	18.7 (2720)
Elongation (%)	530	380
Hardness (Shore A)	50	67
Tear die A, kN/m (pli)	56.3 (320)	33.4 (190)
Mooney at 121°C (250°F)		
Scorch, t5 (minutes)	10	9
Plasticity (ML)	15	28
Compression Set after 22 hrs at 70°C (158°F)		
% set	38	22

Source: R.T. Vanderbilt Company, 1990.

Table 7. Properties of EDPM Hose Compounds

Ingredients	Parts
Highly Extended Hose Compound	
Nordel® 2760P	100.0
Zinc oxide	5.0
Stearic acid	2.0
Oil and Fillers	
Atonite whiting	200.0
GPF black (N-650)	200.0
Cincosol 4240	200.0
Paraffin	2.0
Altax	1.5
Butyl Zimates	3.0
Sulfur	1.0
Vanax A	1.0
Methyl Tuads	1.0
Mooney Scorch, MS 121°C (250°F)	
Minimum viscosity	13
Time to 10 pt. rise (minutes)	17
Vulcanizate Properties, Press Cure, 177°C (350°F), 5 min	
100% modulus, MPa (psi)	2.2 (310)
Tensile strength, MPa (psi)	6.4 (920)
Elongation (%)	460
Hardness (Shore A)	70

Ingredients	Parts
Steam Hose Tube Compound	
Nordel® 2522	100.0
Agerite Resin D	1.5
Zn stearic	1.5
Oil and Fillers	
FEF black (N-550)	55.0
ZnO	5.0
Vanax MBM	1.0
Varox DCP-40C	6.5
Mooney at 132°C (270°F)	
Scorch, t5 (minutes)	6.5
Viscosity (ML)	39.0
Cured 8', 177°C (350°F) Original Properties	
100% modulus, MPa (psi)	4.9 (710)
Tensile, MPa (psi)	13.0 (1885)
Elongation (%)	190
Hardness (Shore A)	74

Source: R.T. Vanderbilt Company, 1990.

Many more examples illustrating the effect of compounding on properties are available in the *Vanderbilt Rubber Handbook* and other similar reference sources. Such reference sources can give guidelines to compounders as a starting point in developing a new compound. They are also helpful in determining the compound properties required for specific applications. In the case of devulcanized rubber, they can offer target properties to determine which applications might be most appropriate.

Properties

When considering the use of devulcanized rubber in various applications, the properties of the rubber are critical to both its processing characteristics and its suitability in the final application. This is true of tires, mechanical goods (belts, hoses, seals, etc.), or lesser applications such as floor mats, insulation, etc. Most of the published data identified in this study has been associated with the following properties: Mooney viscosity (ML-4), tensile strength, modulus, and elongation. While these properties are indeed important, many other rubber properties are equally important in characterizing a rubber.

Another key performance property is hysteresis behavior, which in rubber relates to the amount of heat produced with repeated flexing. Hysteresis is particularly important in tire sidewalls, and it is partly for this reason that natural rubber is a major ingredient in most sidewall compounds. This is because natural rubber has better hysteresis properties than most synthetics.

Two other key properties relating to tire building are tack and green strength. Tack is the extent to which an unvulcanized compound will stick to itself or to another unvulcanized compound. Green strength is the strength of the "green," or unvulcanized, compound. Because devulcanization changes the molecular structure of the rubber, the effect of the devulcanization process on these properties is important.

Other important properties involve the aging properties of a rubber, particularly its oxygen and ozone resistance. Antioxidants and antiozonants are chemicals added to rubber compounds to provide such resistance. Little information has been reported with regard to whether or not these chemicals are removed or destroyed during devulcanization, or whether their effectiveness is reduced, thus making it necessary to add more of them to the devulcanized rubber.

Other processing-related properties are not as easily quantified. The time and temperature required to mix a compound and the amount of energy required for mixing, as well as the curing time and temperature required, are difficult to gauge. Some of these processing characteristics for devulcanized rubber will probably be different from those of virgin rubber of the same type.

Part of the difference is that some portion of the original compound ingredients, including curatives, antioxidants, antiozonants, oil, and fillers, will still be present in the devulcanized rubber. These differences also mean that the quantities of curing ingredients required will most likely be different. For example, how much of the original sulfur remains in the rubber in a chemically active state, and how much was lost? And, how much of the original accelerator and activator is still present and is still chemically active? To the extent that some of these chemicals are still present, less of them will need to be added to cure the devulcanized rubber.

All of the properties mentioned in the preceding paragraphs are critical to how well a devulcanized rubber can be used as a complete or partial substitute for virgin rubber. Therefore, a competent rubber laboratory should test the devulcanized rubber to characterize these properties and determine what compound changes are needed to effect the desired cure, provide the desired properties both for processing and for the cured compound, and provide adequate protection against the effects of oxygen and ozone.

Another critical area of laboratory testing is the determination of how the addition of a proportion of devulcanized rubber to virgin rubber affects the properties of the final blend. For example, how much devulcanized rubber, with lower mechanical properties, can be added before the mechanical properties of the blend are significantly reduced? This will determine the practical limits on the levels of devulcanized rubber that can be used in various applications.

Testing will also help to determine the economic viability of using devulcanized rubber in these applications. Some of the data presented later in this report show substantial reduction in tensile strength with the addition of devulcanized rubber. In other cases, little or no reduction in properties occurs. Such large discrepancies in data show that more work is needed to better understand these effects.

Mechanical properties such as tensile strength, modulus, and elongation are not measured on the pure rubber, but on a cured compound. Consequently, a critical point is that these properties are dependent not only on the rubber itself, but on the amount and type of fillers and extenders used, as well as the state of cure.

For example, a tire tread compound of SBR would have much higher mechanical properties than an SBR carpet underlay compound. Even though the same rubber is used, the tread compound would typically have about 45 to 50 parts of carbon black and 5 to 10 parts of extender oil per 100 parts of rubber. The carpet underlay might have 200 or more parts of fillers, usually clay, calcium carbonate, and possibly even some crumb rubber, and 50 or more parts of oil per 100 parts of rubber. Some hose compounds contain as much as 400 parts of fillers and 200 parts of oil per 100 parts of rubber. Compounds used in rubber matting typically use equally large amounts of fillers, often including crumb rubber.

Another important point is that these "lower-value" products do not use poorer quality rubber, but they use less rubber by increasing the amount of fillers and oil in the compound. Just enough rubber is used to achieve the desired properties, while lower-cost fillers and oils extend the rubber to allow the compound cost to be kept competitive. To use an application of devulcanized rubber, with its lower properties, in these products, a little more rubber (and, thus, fewer fillers) may be necessary in order to achieve the desired mechanical properties. This is another area where laboratory compounding and testing would be needed to determine some of the possible applications.

Chemically or Chemically/Mechanically Devulcanized Rubber

Little information is available in the public domain about the properties of rubber compounds formulated with chemically devulcanized waste tire rubber. Some data that were identified during the course of the study are shown in Table 8. The reported data reflect two different types of chemical devulcanization technologies.

Unfortunately, a detailed accounting of test materials, performance parameters, and conditions is lacking, thus inhibiting the extent of interpretation of the data. Comparisons of data are primarily limited to comparing the properties of virgin rubbers with compounds containing the virgin and devulcanized material at concentrations of about 30 percent devulcanized material. As shown by the data in the table, the properties of the mixtures containing devulcanized material are in general moderately lower than those of their virgin counterparts.

Table 8. Properties of Waste Tire Rubber Devulcanized Using Chemical or Chemical/Mechanical Technology

Generic Technology	Technology Surrogate	Test Rubber Compounds	% Devulc (or Ground) Mat'l	Mooney Viscosity (ML-4 @ 212°F)	Tensile Strength (lbs/in²)	300% Modulus (lbs/in²)	Elonga-tion to Break (%)
Chemical	STI-K Polymers DeLink[a]	NR	0	61.9	4,270	1,987	534
		NR w/devulc NR	30	72.3	4,020	2,151	489
		Virgin SBR (1520)	0	96.6	3,880	3,059	358
		SBR (1520) w/devulc SBR	30	109.2	3,580	2,923	345
Chemical/ Mechanical	LandStar/ Guangzhou Research Institute[b]	NR	100	28.4			680
		SR	100	17.2			514
		AMR[c] Powder (devulc. additive)	100	23.9			640
		Tread Tire Compound[d]	0	20.3			772
			28.6	19.7			628
		Light Duty Truck Tire Compound[e]	0	23.8			536
			28.6	20.5			500

[a] Kohler & O'Neill, 1997.
[b] Howlett, 1999. Basis of data: Xingru, 1997.
[c] AMR is assumed to mean activated-modified rubber.
[d] 50 NR + 30 SR + 20 CIS-BR +40 AMR.
[e] 30 NR + 70 SR + 0 CIS-BR + 40 AMR.

Ultrasonically Devulcanized Rubber

Similar to the case for chemically devulcanized rubbers, CalRecovery found limited data in the public domain related to the performance of mixtures containing devulcanized waste tire rubber. A summary of some performance data is presented in Table 9 for some rubbers used in tire construction. As was noted in the case of chemically devulcanized rubbers, a general diminution occurs in properties of mixtures containing devulcanized rubber versus the virgin equivalents. For the conditions of the University of Akron research, data in the table show the following:

1. Substantial diminution of some properties as percent devulcanized rubber is increased.

2. That the percentage reduction in properties between virgin mixtures and those containing devulcanized product generally decreases as the percentage of devulcanized product is increased.

Table 9. Properties of Waste Tire Rubber Devulcanized Using Ultrasonic Technology

Technology Surrogate	Test Rubber Compounds	% Devulc or (Ground) Mat'l	Mooney Viscosity (ML-4 @ 212°F)	Tensile Strength (lbs/in²)	100% Modulus (lbs/in²)	300% Modulus (lbs/in²)	Elonga-tion to Break (%)
U of Akron	SBR 1848[a]	0		2,415		740	780
	SBR (1848) w/devulc SBR[a]	10		1,075		790	540
	SBR (1848) w/whole train reclaim[a]	(10)		1,940		760	660
	SBR (1848) w/30 mesh buffings[a]	(10)		1,440		780	480
	100% NR (SMR CV60) & 0% SBR (23.5% bound styrene, and Duraden 706)[b]	0		3,263	116		670
	NR (SMR CV60) & 25% SBR (23.5% bound styrene, and Duraden 706)[b]	0		1,885	123		600
	NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)[b]	25		580	123		380
	NR (SMR CV60) & 50% SBR (23.5% bound styrene, and Duraden 706)[b]	0		406	131		390

Technology Surrogate	Test Rubber Compounds	% Devulc or (Ground) Mat'l	Mooney Viscosity (ML-4 @ 212°F)	Tensile Strength (lbs/in²)	100% Modulus (lbs/in²)	300% Modulus (lbs/in²)	Elonga-tion to Break (%)
	NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)[b]	50		363	123		320
	NR (SMR CV60) & 75% SBR (23.5% bound styrene, and Duraden 706)[b]	0		363	145		295
	NR (SMR CV60) w/devulc SBR (23.5% bound styrene, and Duraden 706)[b]	75		276	131		250
	100% SBR (23.5% bound styrene, and Duraden 706)[b]	0		290	152		200
	100% SBR (23.5% bound styrene, and Duraden 706)[b]	100		290	138		180

[a] Boron, et al., 1996.
[b] Adapted from Hong & Isayev, 2002 (pp. 160–168).

Chapter 4. Cost Analysis

This analysis of the costs associated with the production of devulcanized rubber is based on information available in the public domain and on the experience of the members of the project team in conducting similar analyses for a variety of processing systems.

Detailed cost data for devulcanization, and associated technical data as mentioned previously, are sparse in the available literature. Breakdowns of capital and operating costs by cost category are essentially not available. In addition, comprehensive mass balance descriptions are lacking, thus substantially restricting the ability to estimate yield of devulcanized rubber and production of process by-products.

Consequently, cost estimates, when found in the literature, could not be analyzed and judged for completeness, reasonableness, and accuracy. Unit production "costs" found during the performance of the study were typically in the range of $0.20 to $0.50/lb. These costs were inadequately documented. In fact, it was not possible to determine if the costs were all-inclusive or if they included reasonable costs for feedstocks, profit, revenues from waste tire disposal fees, and fees for disposal of process residues.

Given the lack of information in the literature, the CalRecovery team opted to construct engineering cost estimates for devulcanization based on descriptions of devulcanization systems identified during the study and described earlier in the report. The cost estimates are based on a synthesis of information and data from multiple sources for a given generic type of technology; for example, chemical.

The team found that this approach was the best method available for approximating the cost of devulcanization. The team consulted multiple sources of information because no source provided anything approaching adequate information and data that would be needed for a third-party analysis of production cost and system performance. Thus, the estimates of cost given in this section are not for a specific (for example, proprietary) devulcanization technology. However, they should be generally applicable for a group of similar types of technology; for example, chemical. Since the majority of information in the available literature is reported in research and development studies, the cost analysis reflects systems using low (that is, laboratory-scale) processing rates.

The analysis was generally performed by determining the costs (capital and operating and maintenance) of the processes and equipment described in the available literature. The cost analyses were conducted for three technologies that use different processing approaches: chemical, ultrasonic, and mechanical.[*] The key processing elements of each of these technologies have been described in Chapter 3 of this report, and they serve as the primary basis of estimating capital and operating and maintenance costs.

In cases where sufficient equipment or other processing information was not found in the literature, the study team used its professional judgment to complete the processing system design, operating plan, etc. The results of the analysis are presented in Table 10. The processing rates used in the analysis are in the range of 75 to 100 lb/hr, as shown in the table. As a context, if 25 percent of California waste tire crumb rubber production (about 8 million tires per year,

---

[*] Insufficient technical information and data were found during the study to enable reliable cost analyses for other devulcanization technologies.

33

CalRecovery, 2003) were to be devulcanized at 10 plants, the processing rate would be about 2,000 lb/hr.

The data in Table 10 summarize the capital costs and operating and maintenance costs for the technologies analyzed. The data for the capital cost analysis include an allowance for engineering services for the construction of the facility. The information shows that the capital costs for the processes vary from about $92,000 to about $166,000.

Table 10. Estimated Unit Costs for the Production of Devulcanized Rubber

Item	Mechanical	Chemical	Ultrasonic
Capacity (lb/hr)	100	75	75
Capital Cost ($)	92,000	166,000	163,000
O&M Cost ($)	135,000	172,000	136,000
Amortized Capital and O&M ($)	143,000	186,000	150,000
Amortized Unit Cost ($/lb)	0.7	1.2	1.0

Interest rate: 6% per year
Amortization period: 20 years
Refer to Appendix A on page 67 for breakdown of cost estimates.

Similarly, the data in the table indicate that the operating and maintenance costs for facilities of this type range from about $135,000 to $172,000. The operating cost estimates include the cost of crumb rubber feedstock for each of the processes. Based on the relative small size of the facilities, members of the project team opted for including the costs of the rental of a building for processing in operating and maintenance costs. This eliminated the cost of building a structure.

As shown in Table 10, the estimated amortized costs for producing devulcanized rubber are: $1.0/lb for the ultrasonic process, $1.2/lb for the chemical process, and $0.7/lb for the mechanical process. The analysis used an interest rate of 6 percent per year and an amortization period of 20 years. Due to uncertainties represented by the lack of detailed technical data and operating history for the technologies, the accuracy of the cost estimates is +/- 30 percent. As mentioned earlier, these costs reflect production at low capacities.

Some reduction in unit cost would likely occur due to economies of larger scale production. However, estimating reduction in unit cost is difficult because of the lack of data relating to production costs to different levels of throughput capacity for particular devulcanization technologies.

For the size of operations considered in this analysis, labor costs are a substantial portion of the production costs. It is very difficult, however, to estimate the magnitude of any potential reductions in unit labor costs that might occur if processing capacities were increased substantially. All circumstances considered, any estimates of commercial production costs for devulcanization of waste tire rubber are highly speculative at best. The best estimate of the study team is that perhaps production costs could be reduced by 25 to 30 percent if processing capacities were increased by a factor of approximately 5 to 10. Selling prices for devulcanized rubber would also normally include markups for marketing and profit.

The revenue potential of devulcanized material is described in the following section.

Chapter 5. Market Analysis

Devulcanized Grades of Products

The commercial market for devulcanized rubber is at best limited. The market, especially for tire-derived devulcanization, is quite small. There are no industry or common product specifications and grade definitions. Accordingly, there is no consensus on the devulcanization product grades. The companies promoting and developing devulcanization programs use a mechanism that allows a degree of understanding of the material in question. The approach is to specify the devulcanized rubber first by particle size using crumb rubber mesh sizes, and second by the narrowest definition of the original rubber or application; for example, whole tire or buffing. This method of description is incomplete, and devulcanized rubber offerings under these definitions can vary significantly.

Factors Determining Product Characteristics

As described previously, a number of devulcanization process categories (chemical, ultrasonic, microwave, biological, and others), as well as separate processes within each category, are being marketed and/or developed. Presumably, each of these processes yields devulcanized products with unique characteristics and properties that match up differently as blending agents or substitutes for virgin rubber.

Process operating conditions such as temperature, residence time, and other process variables can change the devulcanized rubber characteristics. Thus, the particle size and rubber source product definition is a loose specification for devulcanized rubber that allows substantial differences in product properties from the original rubber, as well as those contributed by the individual devulcanized rubber processes and producers.

The devulcanization industry needs a standard classification method based on analytical results and measured properties. For example, a devulcanized rubber from tire treadstocks, containing natural rubber and SBR, could be analyzed for bound styrene. Such testing would indicate the proportion of SBR in the blend. Products could also be characterized by testing for the degree of devulcanization. As for properties, the rubber could be compounded using a standard recipe, and the tensile strength, modulus, elongation, and hardness could be measured by standard tests. Such test results, along with the source, crumb size, and process, would provide a method of classification, just as the different types of virgin rubber are classified.

The market for devulcanized rubber, particularly the portion derived from crumb tire rubber, remains in a conceptual or early stage of development. The primary devulcanization topics in literature are academic research developments. Other papers on devulcanization were presented to the Rubber Division of the American Chemical Society in 2003.

A few North American companies have been characterized as having devulcanization capability. These include American Rubber Technologies, Inc. (chemical), CCG/PARMA of Canada (chemical), GoodRubber de Mexico SA DE CV (microwave), LandStar Rubber (chemical), TRC Industries, Inc. (thermal/mechanical), and Ultramer, Inc. (ultrasound) (Recycle Research Institute, 2002).

Industry presentations and website content by American Rubber Technologies, LandStar Rubber, and Ultramer in 2004 include the results of comparative testing of virgin rubber with blends of devulcanized rubber. This is the first step in developing customer interest, requests for samples, product qualification, and sales.

Devulcanized rubber is divided into two primary classifications. The first class is a homogeneous devulcanization of a single rubber grade or formulation made of materials such as natural rubbers or synthetic rubbers (butadiene rubber, butyl, EPDM, nitrile, polyisoprene, and styrene-butadiene rubber [SBR]). These materials typically originate as home scrap or recovered manufacturing scrap from rubber producers or fabricators.

The second class is recycled tire crumb rubber that is a non-uniform material composed of a generally ill-defined mixture of dozens of rubber types and hundreds of tire formulations. Certainly, most devulcanized tire rubber producers eliminate trace amounts of steel, fiber, and other contaminants. For some devulcanized tire rubber products, the normal derived tire impurities could also be present. A devulcanized single rubber type has the potential of being reused by blending it into virgin stock of its original application or a wider specification product using the same rubber grade and/or formulation.

This creates at least two problems in practice. The first is that the devulcanized rubber is not turned back to virgin material with common properties. Depending on the process used, process conditions, the material, and the blending level of the devulcanized rubber, most properties will be reduced by a few percent to more than two-thirds of those of the virgin material. In situations where the devulcanized rubber properties are within 10 percent of the original rubber material, blending would seem to be an attractive opportunity that offers the potential of adding a low-cost recycled substitute.

The operative word in blending devulcanized rubber with virgin rubber is potential. Commercial realities come into play. The costs savings cannot always be realized because of transportation costs, the available scrap, or policies of the buyer. The buyer may think the potential or actual liabilities are too high. The best operating model for devulcanizers of single rubber formulation is a dedicated devulcanization line (or long run) of specific rubber. Smaller volumes of single formulations require incurring extra costs for downtime and lost product caused by the cleanout between runs.

Yet another compatibility issue is present for manufacturers of rubber. The scrap rubber available for devulcanization could possibly undergo formulation with fillers, colorants, antioxidants, and a variety of other rubber chemicals to impart certain final product characteristics.

Table 11 represents the breakout of materials in finished tires. Carbon black accounts for 28 percent of the weight and fillers, fibers, and chemicals account for another 16 to 17 percent. When using a devulcanized rubber, the manufacturer has to change its formulation to account for whatever additives, colorants, and fillers remain in the devulcanized rubber. The devulcanized rubber itself and some of its additives and fillers—such as carbon black—presumably add value. These fillers take the place of new additives and fillers that would otherwise be necessary.

The possibility of mixing unidentified non-rubber materials in the devulcanized rubber may be harmful to critical applications such as tires. Other uncertainties are the performance state and concentration of these other constituents that could have been modified in the postconsumer processing of the tire and rubber.

A related issue is the degree to which protective antioxidants and antiozonants break down or lose effectiveness during the life of the tire or other product. Testing and qualification are required to determine whether devulcanized rubber is technically and commercially attractive for the rubber buyer.

Table 11. Composition of Tires

Passenger Tire	Constituents	Common Materials
Natural rubber	14%	Natural rubber
Synthetic rubber	27%	SBR, butadiene rubber
Carbon black	28%	Carbon black
Steel	14%–15%	Steel
Fabric, fillers, accelerators, antiozonants, etc.	16%–17%	Polyester, nylon, aromatic oil, coumarine resin, silica, bonding agent, stearic acid, antioxidant, processing chemicals, sulfur, zinc oxide
Average weight	New 25 lbs, Scrap 20 lbs	
Truck Tire		
Natural rubber	27%	Natural rubber
Synthetic rubber	14%	Synthetic rubber
Carbon black	28%	Carbon black
Steel	14%–15%	Steel
Fabric, fillers, accelerators, antiozonants, etc.	16%–17%	Polyester, nylon, aromatic oil, stearic acid, antioxidant, wax, processing chemicals, sulfur, zinc oxide
Average weight	New 120 lbs, Scrap 100 lbs	

Source: Rubber Manufacturers Association, 2004.

Market Situation

Only a few companies devulcanize single formulation rubber by tolling, captive conversion, or merchant scrap recovery from manufacturing. The production of devulcanized rubber from home manufacturing scrap ranges from 100 to 200 million pounds annually, which represents about 1 to 2 percent of total U.S. rubber consumption. The largest volume devulcanization activity supports the domestic tire and rubber companies.

Examples of devulcanized rubber are butyl, EPDM, fluorosilicone, natural, nitrile, SBR, and silicone. The group of home scrap reprocessors is not devulcanizing tire rubber with its mix of rubbers, fillers, and additives. Devulcanized rubber supplies only 15 to 20 percent of the rubber manufactured scrap market. The reasons for the limitation of recycled content are primarily difficulty of creating manufactured product of uniform quality and difficulty of reprocessing certain rubber formulations.

TRC Industries uses a proprietary steam/mechanical devulcanization process. TRC claims the devulcanized material will retain all of its original physical properties and characteristics. The degree of devulcanization typically is in the 70 to 80 percent range and is occasionally 100 percent. Heavy carbon-blacked rubber is the hardest to devulcanize, and silica, or other mineral-filled EDPM, is the easiest. Reincorporation of the devulcanized rubber is typically in the 20 to 40 percent range.

Devulcanized single-product rubber applications are wide ranging. The reclaimed product may be reintroduced into the same end product or one with more tolerant performance characteristics for the devulcanized rubber. Examples of applications using devulcanized rubber are tire bladders,

seat spring covers, mounts, various molded goods, matting, and foam crack sealer. While many of these devulcanization operations of manufacturing scrap are tolling or captive processing, value of the scrap is priced effectively at a discount to virgin rubber in the 20 to 50 percent range. The reprocessing of home scrap requires a location in proximity to a large volume scrap generator.

Significant growth for devulcanized single rubbers depends on continuing process development of the reclaiming operation as the manufacturers strive to reduce operational losses. The supply stream from existing scrap applications will over time decline as scrap from these operations is reduced by manufacturing improvements. Increasing the volume of single rubber scrap for devulcanization processing requires adding new sources of rubber for reuse and developing ways to process them.

Companies developing the market for devulcanized tire rubber would first use more uniform types of rubber or tire component. These include buffings (tire tread or other portion of the tire free of metal or fiber; usually removed in preparation for retreading), peels (tire separations; usually the portion of the tire retread that has separated and been left on the highway), or truck tire sections with a high, natural-rubber content.

Using a whole tire mixture of rubbers introduces especially wide devulcanization product specifications and performance variations. Whole tire devulcanized rubber is at the low end of supply quality for each market application. Despite ongoing research and business promotion of devulcanized rubber, industry observers note slow sales of devulcanized tire rubber. Feeding an inconsistent supply of devulcanized rubber is less interesting for the buyer than a guaranteed, stable supply. This may be one of the larger market restraints on the success of waste tire devulcanization.

Replacement treads for some vehicle tires are made of undevulcanized crumb rubber (American Rubber Technologies, 2004). Devulcanized rubber seems to have advantages in bonding, strength, and tread integrity above the properties of crumb rubber, which acts only as a "rubber"-like filler. The unknown factor is cost, which could prevent devulcanized rubber from being used in many retread rubber applications.

Regardless of the actual level of commercial success for devulcanized tire rubber, no industry grade definitions are available. Developers of devulcanized tire rubber described their products in terms of crumb rubber mesh sizes and the narrowest form of use for the original rubber that might apply, such as buffings or whole tire. Purchasing guidance is provided on the devulcanized tire rubber, but not a uniform specification. The lack of a standard specification creates uncertainty for the buyer.

The type of devulcanization process, and process conditions, will cause variations in devulcanized tire rubber products. Other factors causing variation include composition of the mixture of scrap tires or tire components processed, and quality control of the devulcanization process. The quality of a single type of devulcanized rubber scrap will also have inherent variation introduced by the devulcanizing process and operating conditions.

Devulcanized Rubber Product Characteristics

No data are available comparing devulcanization processes or the offerings of one company to another. The available data in the public domain is predominantly in research and development, with available commercial data doubling as sales literature for promoting devulcanized rubber. The physical property data presented in Table 12 are referenced by source. Comparing devulcanized rubber properties leads into the next section in this report, "Devulcanized Rubber Prices."

Table 12. Percent Change from Virgin with Selected Devulcanization Rubber Formulations

Test Rubber Compounds (grade) Parts or %	% Devulc. or (Ground) Mat'l.	Hardness Shore	Tear Strength	Tensile Strength	100% Modulus	300% Modulus	Elongation to Break
Chemical							
STI-K Polymers DeLink[a]							
NR w/devulc NR	30			-5.9%		8.3%	-8.4%
SBR (1520) w/devulc SBR	30			-7.7%		-4.4%	-3.6%
Kyoto University[b]							
Truck tire (93 NR+ 7 BR)							
84 NR+ 6 BR + 20 devulc	18	8.1%		-2.3%	2.6%		0.0%
74 NR+ 6 BR + 40 devulc	33	12.9%		-11.9%	28.2%		-17.4%
65 NR + 5 BR + 60 devulc	46	11.3%		-19.1%	23.1%		-13.0%
LandStar/Guangzhou R I[c]							
100 SIR 10 + 50 devulc							
SIR vs. Case 1	33	4.3%		-23.7%	6.7%		-6.7%
SIR vs. Case 2	33	6.5%		-23.0%	11.5%		-8.6%
Tread Tire Compound							
50 NR + 30 SR + 20 CIS-BR +40 AMR	28.6	6.7%	-17.3%	-3.0%			-18.7%
Light Duty Truck Tire Compound							
30 NR + 70 SR + 0 CIS-BR + 40 AMR	28.6	1.6%	-10.9%	-13.9%			-6.7%
Retread Tire Compound							
[c]65 NR + 35 SR +40 AMR	28.6	6.3%	-8.6%	-10.3%			-16.8%
Ultrasonic							
University of Akron[d]							
Versus Akrochem SBR (1848)							
SBR w/devulc SBR	10			-55.5%		6.8%	-30.8%
SBR w/whole Tire Reclaim	10			-19.7%		2.7%	-15.4%

Test Rubber Compounds (grade) Parts or %	% Devulc. or (Ground) Mat'l.	Hardness Shore	Tear Strength	Tensile Strength	100% Modulus	300% Modulus	Elongation to Break
SBR w/30 Mesh Buffings	10			-40.4%		5.4%	-38.5%
Natural Rubber and SBR versus devulc							
Base 100% NR (SMR CV60) & 0% SBR (23.5% bound styrene, and Firestone Duraden 706)[e]	0						
Add 25% SBR, 75% NR	0			-42.2%	6.3%		-10.4%
Devulc SBR replaces SBR							
25% devulc SBR, 75% NR	25			-69.2%	0.0%		-36.7%
50% devulc SBR, 50% NR	50			-10.7%	-5.6%		-17.9%
75% devulc SBR, 25% NR	75			-24.0%	-10.0%		-15.3%
SBR versus devulc SBR							
100% devulc SBR	100			0.0%	-9.5%		-10.0%

[a] Kohler & O'Neill, 1997.
[b] Kyoto Chemical Research Institute, 2002.
[c] Howlett, 1999. Basis of data: Xingru, 1997.
[d] Boron, et al., 1996.
[e] Hong & Isayev, 2002 (pp. 160–168).

The devulcanized rubber properties displayed are not necessarily optimized for a specific end use. Formulators will likely be able to incorporate devulcanized rubber along with other formulation components to achieve a higher level of final product performance. Key product performance variables are level of contamination, number of rubber types in the rubber mixtures, and additives used by the formulations. The effect of additives was discussed previously under "Product Characteristics." The number of types of rubber in waste tires is one of the most important factors affecting quality of devulcanized waste tire rubber. Optimizing a devulcanization process is very difficult when more than one type of rubber is involved.

Blend Rates

According to one developer of a devulcanization process, about 3 to 10 percent of the final product can be blended into virgin material before performance properties are affected (Rubberworks International, 2004). Variations of a few percent are reported by developers of devulcanization when they vary process run conditions (Howlett, 1999). Run-to-run variations are

normally acceptable. Another firm that is developing devulcanized rubber placed the breakpoint for noticeable performance change at 10 percent, reasoning that customers typically allow a 10 percent variation in product from the purchasing specifications (Thomas, 2004).

The descriptions of properties for a common grade of virgin rubber from two producers vary by 7 to 20 percent (Boron et al., 1996; International Specialty Products, 2004). With this much variation in the marketplace, devulcanized rubber is expected to find technical acceptance increasing. This will happen as the devulcanized product property variance from virgin rubber falls from above 20 percent to less than 5 percent.

Performance Properties

The key point of Table 12 is that devulcanized rubber is not the same as virgin rubber. Thus, the extent of variation and the specific characteristics will be important determinants in the acceptance and value of devulcanized rubber versus virgin rubber. The data points of Table 12 demonstrate that devulcanized single rubber products have a much lower degree of degradation than multiple rubber mixtures with devulcanized rubber. Virgin single-grade SBR—or natural rubber replacement with devulcanized material shown by the STI-K and the University of Akron datasets—has, at worst, a reduction of 10 percent in tensile strength, modulus, or elongation.

Based on the results shown in Table 12, the properties of the single rubber compounds with devulcanized material are within normal grade tolerances. These single rubber compounds seem likely to have some market application, if not restrained by cost. The performance properties of multiple compound formulations—when replaced by devulcanized tire or single rubber grade— are lowered, with at least one property dropping by 15 percent or more.

The Kyoto University tests show that progressively increased devulcanized material in the formulations resulted in a steadily poorer match with virgin rubber. University of Akron data indicate weakening properties with increasing additions of devulcanized rubber. While not uniform with each step of increased concentration of devulcanized SBR, devulcanized rubber consistently performed at a level below that of virgin SBR.

In some cases, the addition of devulcanized rubber causes a major reduction in performance of some properties, along with improvements in one or two properties (hardness and modulus). Because the modulus is the measure of deformation—that is, tension (stretching), compression (crushing), flexing (bending), or torsion (twisting)—a higher reading means a stiffer product that may or may not be desirable. Similarly, the increase in hardness could be an improvement or detraction, depending on the application. Because each use has its own measures of desired performance, generalizations about acceptability are not appropriate. This is extremely important. Increase in modulus and/or hardness is quite often accompanied by decrease in strength and elongation, quite possibly making the rubber unsuitable for use in the normal applications of that type of rubber.

Development Status

Rubber devulcanization processes have been in development for more than 60 years (Baker, 2003). The research goals continue to seek processes that offer a better combination of the cost of devulcanizing the rubber and properties compared to virgin material. The processes in Table 12 are a sample of many development programs that are reportedly still in consideration or active. STI-K Polymer offered the De-Link chemical process that was first introduced into the United States about 1995.

This company has apparently closed its office in Washington D.C., but it remains listed on www.recycle.net/. American Rubber Technologies (ART) is reportedly licensed to the De-Link

process. ART employs the brand name ReVived Rubber® for its devulcanized rubber. ART adopted the process in 1997, producing partially devulcanized output. ART claims that devulcanized particle sizes that are twice as large as crumb rubber work as well or better. ART continues to promote ReVived Rubber®; however, it may have reduced its devulcanized rubber sales effort. CCG/Parma has offered the STI-K Polymer process in Canada and reportedly has the capability to make devulcanized rubber as well.

Kyoto Chemical Research Institute at Kyoto University is actively reporting research findings on its supercritical CO_2 devulcanization process. A commercial partner was not identified.

LandStar Rubber licensed the Guangzhou R I chemical devulcanized process in 1999. This company has emphasized devulcanized rubber products as it grew its tire recycling business by acquisition and more recently as it scaled back operations. The LandStar company name was changed by adding the word "rubber" to reflect its focus on devulcanized rubber. The company is now reportedly protected in a bankruptcy proceeding.

University of Akron Professor A.I. Isayev is one the founders of modern rubber devulcanization. His team appears to be the most active of the research teams, based upon many papers reporting results for more than a decade. The focus of the University of Akron research is ultrasonic devulcanization. Ultramer, Inc., a subsidiary of NFM/Welding Engineers, Inc., is participating in the development of this devulcanization process; however, development efforts appear to have lessened recently.

Several California companies, such as Redwood Rubber LLC, Tires2Oil, POLYMERight, and Champion Rubber Products, have been researching and developing devulcanization technologies at various levels of effort.

The apparently limited commercial success of these processes is not highly encouraging for the probable future prospects of marketing devulcanized rubber. Devulcanizing waste tires may be a technology with a bright future, but no success stories on this process are currently available.

Devulcanized Rubber Prices

The devulcanized rubber market is not developed enough to have established prices. Even the few devulcanizers that are reclaiming manufacturing scrap in large volume view each supply agreement as a special case. The manufacturing customers have differing purchasing specifications, liability concerns, environmental drivers (recycling can be a positive public relations boost), disposal costs, and product mixes that are able to adsorb devulcanized rubber as "off spec" virgin. The pricing issue is further confused by the internal pricing of captive devulcanizing operations.

Substitute Pricing

The virgin natural and synthetic rubber prices are ultimately driven by the volatile supply and demand effects of the agricultural crop, natural rubber, and energy prices. The synthetics are petrochemical-based materials. Devulcanized rubber competes with virgin rubbers. Thus, its market price is influenced by natural and synthetic rubber. Figure G illustrates the natural rubber volatility.

The natural rubber price trend line (spot price for ribbed smoked sheets, Grade No. 1, New York) from 1980 to 2003 had an average annual rate of decline at 0.5 percent/year. However, during this same period, the natural rubber price experienced four declines and five peaks. These fluctuations averaged 15 to 18 percent, respectively, beneath and above the trend line. The fluctuations in the relative prices of natural and synthetic rubbers do affect consumption. When natural rubber has a

price spike such as that of 1995 to 1996, rubber product producers will change their compounds to use as much synthetic rubber as they can without sacrificing product performance. Likewise, when natural rubber prices are low, such as in 1999 to 2001, natural rubber consumers will use more product.

Figure G. Natural Rubber Prices Show Volatility

Ribbed Smoked Sheet 1, Spot Price, New York
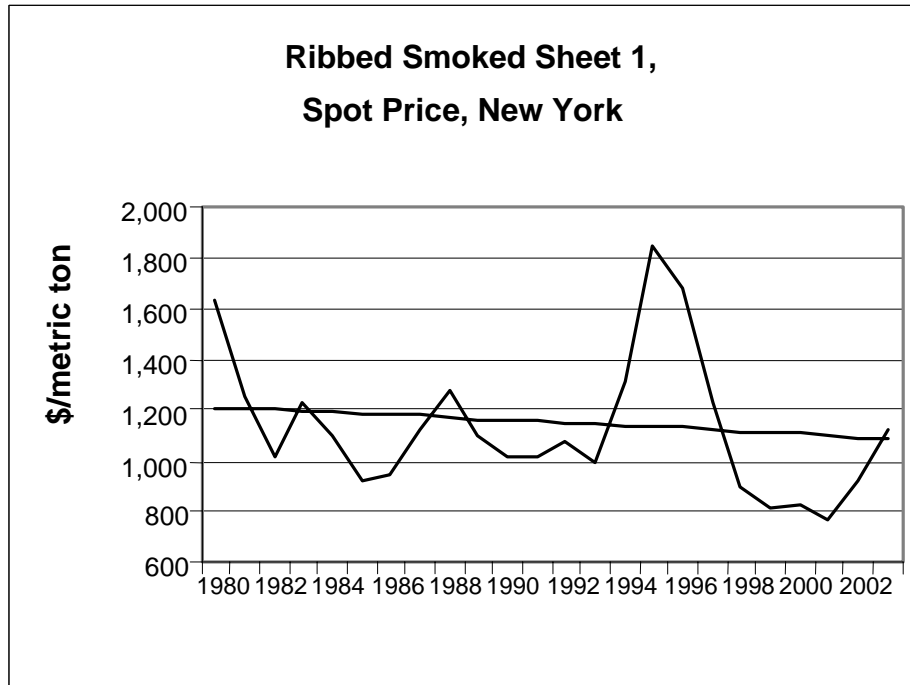
International Rubber Study Group, 1982–2003.

Table 13 shows that rubber prices have traded in a narrow range in the period from 1999 to 2002. The prices of virgin rubber and crumb rubber begin to bracket the expected price for devulcanized rubber. The synthetic rubbers, SBR and butadiene rubber, are both major elastomers used in tires.

To simplify the estimate, unit imports values are used as a proxy for the market price of the virgin rubber. The actual market price of large buyers and sellers is very difficult to estimate without inside knowledge. The unit value for large shipments can be a reasonable representation of the market price for a high level evaluation. SBR and butadiene rubber have price spikes with market shortages. Nevertheless, the annual import values for SBR for the period of 1999 to 2002 were within 8 percent of the 44.8 ¢/lb average over the seven years. Butadiene rubber annual import unit values were within 15 percent of the 41.9 ¢/lb average.

Table 13. Price and Unit Values (¢/lb)

		2002	2001	2000	1999
Natural Rubber					
TSR 20[a]	Import Unit Value	30.3	27.5	31.7	27.2
RSS 1[b]	Import Unit Value	33.3	30.2	31.9	29.8
Synthetic Rubber					
SBR[c]	Import Unit Value	47.2	47.3	44.2	41.5
Butadiene Rubber[d]	Import Unit Value	39.6	45.5	40.8	36.4
Crumb Rubber, Average[e]					
	10 Mesh	13.3	12.7	12.4	12.1
	20 Mesh	14.9	14.9	15.2	14.7
	30 Mesh	17.3	17.3	17.8	17.5
	40 Mesh	21.0	21.0	22.0	20.6
	80 Mesh	31.0	31.0	30.8	29.2

[a] General Imports (Harmonized Trade Code 4001220025: Technically Specified Natural Rubber, Grade 20), United States International Trade Commission, 1997–2002.

[b] General Imports (Harmonized Trade Code 4001210010: Natural Rubber In Smoked Sheets, Grade 1), United States International Trade Commission, 1997–2002

General Imports (Harmonized Trade Code 4002190010: Styrene-Butadiene Rubber (SBR);

[c] General Imports, Carboxylated Styrene-Butadiene Rubber (XSBR) Containing 50% or Less Styrene by Weight of the Dry Polymer), United States International Trade Commission, 1997–2002.

[d] General Imports (Harmonized Trade Code 4002200000: Butadiene Rubber [BR]), United States International Trade Commission, 1997–2002.

[e] Recycle Research Institute, 2002.

Recycle Discount

Recycled materials have no common pricing rules. These markets are driven by the overall supply and demand for a specific material or substitute, with very wide price swings possible. The practice of determining value for recycled plastic and fiber, as well as devulcanized manufacturing scrap rubber, suggests a range of discounts from the virgin material. Manufacturing scrap of fibers and plastics can sometimes be reused directly or reused in the same application with reprocessing.

The value of the recycled fibers and plastics can vary substantially, with discounts of 20 to 50 percent or more off the virgin material price. Compared to single compound or tire rubber processing, plastic and fiber recycled materials are only slightly degraded by the recycling process. Accordingly, except in special cases, discounts from virgin material of at least 20 to 50 percent would be considered reasonable for devulcanized tire rubber. With tightness or weakness in the market, the discounts off the price of virgin rubber can shift throughout a wider range.

Market Value

Single composition rubber devulcanization will follow its own market dynamics, establishing an appropriate unique product discount. Most single devulcanized rubber transactions are expected to be discounted in the 20 to 50 percent range. The United States unit import value is a proxy for the market price of natural rubber, SBR, and butadiene rubber.

Devulcanized tire rubber has a cost relationship with its raw material, crumb rubber. Crumb rubber prices have remained fairly steady because its cost structure is based on the low to negative value of surplus tires. The surplus tire situation and valuation of waste tires are not expected to dramatically change in the foreseeable future.

Crumb tire rubber (20 to 80 mesh) is the main raw material for devulcanized tire rubber. Crumb rubber will act as the price foundation, with an appropriate upcharge for the process of devulcanizing rubber. From 1996 to 2002, the average price for mesh 20 to 80 crumb rubber grew at an annual average of less than 1 percent, with little year-to-year variation.

The high and low crumb prices of 80 mesh varied from 7 to 31¢/lb in 2002. This spread has narrowed significantly during the past four years, probably reflecting an increased ability of crumb rubber producers to make the small mesh sizes. The average 20 to 40 mesh prices have been particularly flat during the past four years (Sunthonpagasit & Hickman, 2003). Crumb rubber prices were reported to be flat from 1994 to 2000 because of oversupply of crumb rubber and other factors.

The following demonstration case illustrates the price relationship of virgin rubber to crumb rubber and creates a range of expected prices for devulcanized tire rubber. A discount for using a recycled product is applied to the virgin rubber price and becomes the high expected value for devulcanized tire rubber. The low expected value for devulcanized tire rubber is based on the cost of crumb rubber and the devulcanization process costs. Prices between the high and low expected values establish the most likely range for devulcanized tire rubber prices.

Table 14 presents values that will be the basis for estimating the foundation level for devulcanized rubber pricing based on crumb rubber and the ceiling for devulcanized rubber based on a discount off virgin rubber prices. The actual floor for successful devulcanization operations is the crumb rubber price plus a markup for the reclaiming operation.

Table 14. Bracketing of the Expected Devulcanized Rubber Price (¢/lb)

	2002	2001	2000	1999
Tire tread rubber price (50% NR + 30% SBR + 20% BR)	38.0	37.7	37.3	34.0
Less 20% discount from virgin	30.4	30.2	29.8	27.2
Less 50% discount from virgin	19.0	18.9	18.7	17.0
Average crumb rubber price + devulcanization upgrade (+10 ¢/lb)	33.1	33.1	33.5	32.4

Based on Table 13.

A cost basis for devulcanized tire rubber can be approximated by taking the crumb rubber price and adding an estimate for commercial-scale devulcanized rubber processing.[*] For this particular analysis, assume that the cost of devulcanization is in the vicinity of 10¢/lb. This optimistic figure represents a five- to tenfold improvement over the cost estimate derived in the previous section. Under this assumption devulcanized rubber is competitive if the average of the 20 to 40 mesh crumb rubber was taken for 2002 at 23¢/lb. Adding the assumed 10¢/lb for additional processing creates an estimated cost for devulcanized tire rubber of 33¢/lb in 2002.

As shown by the data in Table 14, the applicable potential margin for devulcanized tire rubber would likely squeeze producers. The following demonstration case calculates the value of a type of devulcanized tire rubber made partially of virgin rubbers. The tire tread formulation use for this case is 50 percent natural rubber, 30 percent SBR, and 20 percent butadiene rubber (the same ratio as used by LandStar in comparing its devulcanized rubber to virgin rubber).

To be truly competitive, the selling price of devulcanized rubber would need to be at or below the ceiling prices established by the 20 to 50 percent discount off the weighted average price of rubber in the tire tread formulation. In 2002, a 20 percent discount on the virgin rubber price yields a ceiling price for devulcanized tire rubber of 30¢/lb. This 30¢/lb ceiling price is below the minimum estimated production cost of 33¢/lb that was computed earlier.

With different cases and assumptions, the devulcanized tire rubber might fall into a range likely to offer commercial potential. Applications that are well matched to properties of devulcanized rubber would lower the expected recycling discount. If crumb rubber and/or devulcanization processing had a lower cost—for example, below average crumb rubber costs—its prospects look more promising. The reported high to low price range in 2002 for crumb rubber mesh sizes from 20 to 80 are 7¢ to 16¢/lb, and the low to average range is 3¢ to 9¢/lb. The variation reflects quality, distance to market, and end use differences.

The tire tread example discussed here is built on many assumptions. The best way to determine the acceptance of devulcanized rubber and its selling price is to test devulcanized tire rubber in the marketplace. Only a business development effort can pinpoint a set of costs and expected value based on product properties for devulcanization material. Potential customers can verify these costs in turn.

The above example leads to speculation about why devulcanized tire rubber has not made a greater impact. Selling crumb rubber may be more attractive than the potential benefits resulting from the extra processing of devulcanization. The crumb rubber markets are now better defined, but the missionary work necessary to develop devulcanization applications is another drain on company resources. Tire recycler/crumb rubber producers are generally very lean organizations. Devoting resources to a long-term effort necessary to build devulcanization sales is relatively expensive, especially if the anticipated return is modest or negative.

---

[*] In all cases for devulcanized rubber value, credit for non-rubber constituents is assumed to be valued at the same price as the rubber. A detailed investigation could refine the estimate in this study to adjust the value of the rubber by the price and weight of non-rubber compounds. The actual value impact of carbon black, fillers, and rubber chemicals will depend on usefulness of these chemicals in each application of the devulcanized rubber. For situations where any or all of these non-rubber ingredients are not required, the buyer might not offer any value or assign a negative value. In most situations, the pricing of the devulcanized rubber could be further adjusted by using concentrations of significant chemicals and fillers that make up the product. Dozens of grades of carbon black could be commingled in devulcanized rubber. Carbon black, the other major material present in crumb rubber, has sold in the range of 35¢ to 50¢/lb, in approximately the same range as that of virgin rubber. The price of stearic acid is usually below that of the virgin rubber. Zinc oxide sells at a significantly higher price.

This simplified analysis has ignored distinctions created by different devulcanized rubber processes presumed to have unique properties with special pricing needs. Each process could conceivably have its own cost structure, reflecting the tradeoff between product properties and market prices.

Therefore, each different production process will probably have different market coverage and competitive strength. ART quoted a price of 30¢/lb for its fine grade and 37¢/lb for its super-fine grade. In the tire tread example, this fine grade is approximately at the 20 percent discount level. The quoted price for super-fine devulcanized rubber is only a penny a pound below the composition virgin rubber tire tread price, which will probably be a tough sell. Buyers under the right conditions might consider devulcanized rubber at a discount less steep than 20 percent.

The commercial market for vulcanized rubber includes a wide variety of rubber compounds and formulations being used in thousands of different applications. Whatever the market condition, rubber purchasing specifications may very well be a good match for devulcanized tire rubber in some niches. But, finding these special circumstance market niches could be challenging. Thus, the long-term opportunities for devulcanized rubber remain unclear. Companies engaged in developing devulcanized tire rubber have not yet reported large-scale commercial success, leaving a pessimistic outlook.

The Demand for Devulcanization

Single Composition Devulcanized Rubber

Single compound home scrap devulcanization is currently almost a captive market. The few participants are located in Ohio, Texas, and the southeast United States. The companies are captive suppliers or are selling (tolling) back to their raw material suppliers. Thus, the market is not fully open to competition. These devulcanizers have a large volume scrap which can be processed close to its source—an unusual situation.

The existing available market is growing at less than the underlying pace of the industry. The amount of scrap generated by rubber companies is probably declining as management of their operations improves. Because only 15 to 20 percent of the scrap is being reprocessed, considerable high-side potential exists for the single compound devulcanization industry. This potential will be available if these businesses can expand the use of devulcanized rubber into a new and better process technology.

A potentially large single-composition devulcanized rubber market will exist for the foreseeable future as long as the devulcanization technologies continue to improve. The 100 million pound-plus market will grow at least as fast as the rubber industry (less than 3 percent annually) and is likely to significantly outpace the industry with technology and product innovations.

Devulcanized Tire Rubber

Determining the future demand for devulcanized tire rubber is more difficult, since the present products and markets are so ill defined. After years of development, devulcanized tire rubber is still seeking a market. The reasons may be economic, coupled with the difficulty of doing long-term market development with a base in the recycled rubber business.

The devulcanized tire market is divided between partially and fully devulcanized processes. Neither partially or fully devulcanized tire rubber has a significant established market. A portion of the crumb rubber used for asphalt paving operations is devulcanized. Caltrain has a provisional specification for paving material to incorporate crumb rubber. While most crumb rubber being used in asphalt is not devulcanized, a very high-end asphalt product consumes relatively large

amounts of crumb rubber that is "reclaimed" in the process. This crumb rubber application is ignored when looking at the demand of devulcanized rubber.

No devulcanized tire rubber applications were identified. Devulcanized rubber should, under the right conditions, replace crumb rubber in applications where it is more compatible with vulcanized rubber. Compared to virgin material, devulcanized rubber may offer a discount price for the cost-conscience buyer.

The devulcanized tire rubber is expected to find a market in molded goods, binders for plastics, and applications needing a better surface finish. Examples of product areas are footwear soles, rubber sheeting, car mats, tire carcass, and inner liner compounds. Others include tread and sidewalls of tires, flaps, belts and hoses, other automotive molded parts, other manufacturing high-quality molded parts, gaskets, extruded profiles, rubber strips, and caster wheels.

Companies such as Ford and Kumho have each set 10 percent goals for recycled material in their tire formulations. Devulcanized rubber has an obvious compatibility advantage over crumb rubber, which is merely a filler. No development program using devulcanized rubber in tires was found. Therefore, establishing a successful program in the commercial sphere is probably at least three to four years in the future if program development begins immediately.

Development delays are created by lags in the preparation for automotive model years. Ford and Bridgestone, as well as the other automotive and rubber tire companies, are very likely to be methodical in looking at uses for new material. They know the risk of mistakes such as the Ford Explorer tire failures that hurt both Ford and Bridgestone financially and organizationally.

Tire devulcanizers are not well equipped to start a recycled rubber campaign aimed at capturing a major share of the rubber needs of tire companies. Such an effort would be both expensive in time and capital resources for the size of their businesses. Should the United States institute a 10 percent devulcanized rubber requirement for U.S.-manufactured tires, the demand for devulcanized rubber would exceed 500 million pounds annually. This is more than half the present North American market for all crumb rubber.

This potential demand is so large that even the major rubber or auto companies would have to move slowly into its implementation. Recycling tire rubbers into new tires remains an interesting market. However, this is a very difficult path for individual devulcanizers. They are much too small, with too few resources.

California

California has a well-developed growing market for rubber. The state is the home to one of the largest regional business activities for rubber products in the United States, as is shown in Table 15. The 1997 California sales share of the U.S. total manufactured rubber products, tires and treads, and other rubber products was 4 percent, 3 percent, and 5 percent, respectively. Sales of all rubber products manufactured in California totaled $1.4 billion. This represents a major rubber market. California is the largest crumb rubber market in North America, by far. California had about 17 percent of the crumb rubber production of the United States and Canada, despite a significant dip in 2002. With this large volume of crumb rubber in the state, it could, under the right circumstances, lead California to be a major force in the development of devulcanized rubber.

Table 15. 1997 Role of California in the United States Rubber Product Manufacturing Sector

Type	Area	Establish-ments	Sales $000	Payroll $000	Employees
Non-Tire Rubber Products	United States	1,898	19,016,832	3,812,770	130,164
	California	221	997,516	214,000	8,253
	California %	11.6%	5.2%	5.6%	6.3%
Tire and Retread	United States	911	15,699,140	2,962,564	72,189
	California	78	415,452	63,328	1,855
	California %	8.6%	2.6%	2.1%	2.6%
All Rubber Products	United States	2,809	34,715,972	6,775,334	202,353
	California	299	1,412,968	277,328	10,108
	California %	10.6%	4.1%	4.1%	5.0%

Source: U.S. Department of Commerce, 1997.

The role of devulcanized rubber in the future for California is unclear, as it is elsewhere. The market analysis of the U.S. situation is uncertain because the base case economics require the development of new, undefined markets with below-average cost and/or less discount than is typical in the rubber and plastics industry for recycled material.

The California market potential for devulcanized rubber, particularly tire rubber, has advantages over most other North American locations. California has a major share of crumb rubber production, which is the starting material for devulcanized rubber. The state also has a major rubber products industry that could become a devulcanized rubber consumer. What appears to be lacking in the marketplace are applications that can make the best of the properties of devulcanized rubber while still benefiting customers with discounts off of virgin rubber prices. The identification of these applications will take some creative thinking to match devulcanized rubber strengths with unmet market needs.

Chapter 6. Environmental Analysis

Introduction

Little information is available in the literature on the environmental effects associated with waste tire devulcanization technologies. The lack of information apparently exists because business developers and researchers have concentrated their efforts primarily on technology improvements and achieving satisfactory properties for devulcanized rubber. Since reported data are lacking from actual devulcanization systems, an estimation of emission rates and a detailed environmental analysis are not possible.

However, using data and information from some other types of tire manufacturing processes (for example, extrusion of rubber) and the characteristics of vehicle tires, the CalRecovery team performed a qualitative analysis. The main purposes of the analysis are to describe the potential environmental impacts of waste tire devulcanization systems, the types of environmental regulations that might or do apply, and the types of environmental control systems that might be required for commercial-scale operations.

The environmental analysis described subsequently is limited to chemical and ultrasonic devulcanization processes because technical information is sufficient for a qualitative evaluation. The need for, and extent of, environmental control is a strong function of uncontrolled concentrations and/or mass flow rates of harmful emissions. The analysis assumes that control of emissions would be required. This condition is invoked in the analysis in order to illustrate the types of potential environmental emissions and potential means of controlling them if such control would be required. The waste tire devulcanization operations identified in the study were primarily small-scale processing operations. These operations may fall below regulatory thresholds for allowable emissions.

The analysis below describes potential environmental impacts of waste tire devulcanization and methods of controlling them. The methods described are meant to be illustrative of those that might be chosen and used; other methods of control might also feasible.
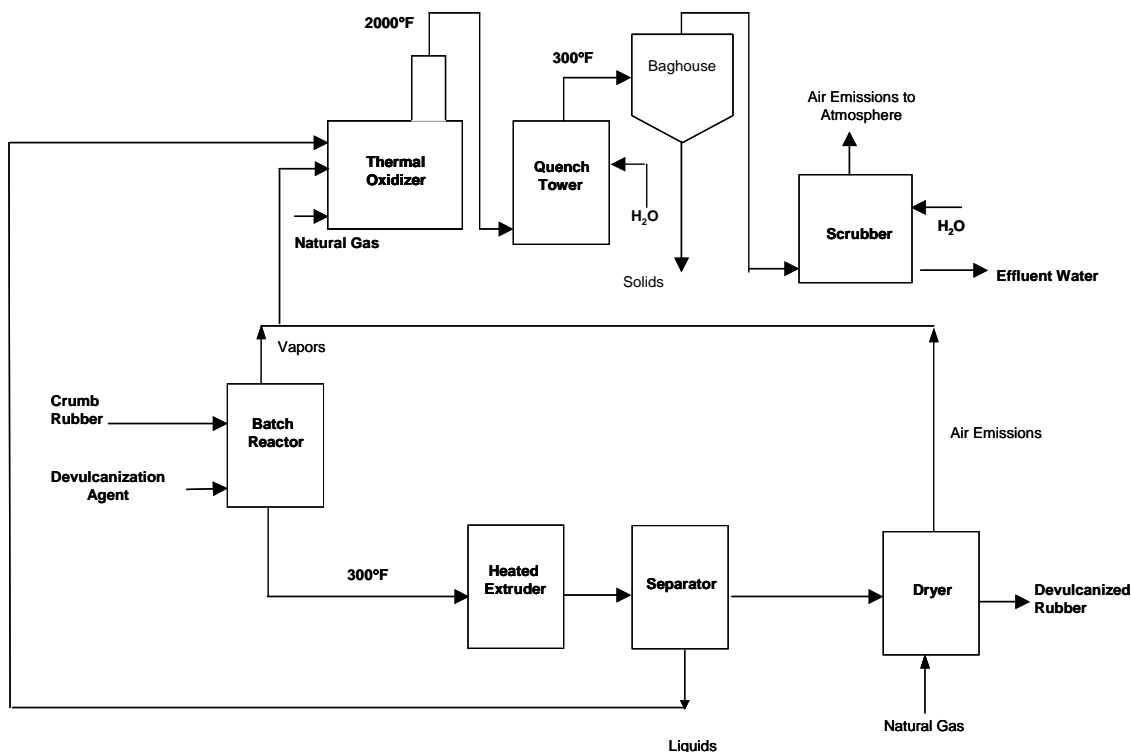
Analysis

Chemical

Chemical devulcanization processes are usually batch processes that involve mixing crumb rubber with chemical reactants at a specific temperature and pressure. Once the design reaction time has elapsed, the contents are then rinsed, filtered, and dried to remove any remaining unwanted chemical components. The product can then be bagged or otherwise processed for resale. A block flow diagram of a generic chemical devulcanization process is illustrated in Figure H, showing the raw material feed is crumb rubber.

The typical constituents of the crumb feedstock generally would consist of those listed in Table 16. The crumb rubber is mixed with one or more devulcanization agents. Chemical agents identified as devulcanization agents are listed in Table 17. During processing in the batch reactor, vapors are released that must be collected and treated before release to the ambient atmosphere. Typical types of vapors that might be emitted from a batch reactor are listed in Table 18.

The chemicals that would be vented from the batch reactor are dependent on the characteristics of the waste tire feedstock and on the chemical agent(s) used in devulcanizing the crumb rubber. For example, if disulfides are used in the process, they could result in formation of hydrogen sulfide (H_2S) or methyl or other mercaptans (RSH).

Figure H. Block Flow Diagram of a Chemical Devulcanization System

Table 16. Tire Raw Materials

Polymers	Antiozonants
Natural Rubber (polyisoprene)	2,2,4-trimethyl-1,2-dihydroquinoline (polymer)
Styrene-Butadiene Rubber (SBR)	n,n-(1,3-dimethylbutyl)-p-phenylenediamine
cis-Polybutadiene copolymer	paraffinic wax
Vulcanizing Agents	**Antioxidants**
Sulfur	Alkylphenols
Tetra-methyl thiurame sulfide	Resorcinol
Accelerators	2,6-Diterbutylhydroquinone
Diphenylguanidine	**Retarders**
2-Mercaptobenzothiazole	n-Cyclohexylthiophthalimide
n-Cyclohexyl-2-benzothiazolylsulfenamide	**Plasticizers**
2-(n-Morpholinyl)-mercaptobenzothiazole	Aliphatic oil
Hexamethylenetetramine	Aromatic oil
Activators	Naphthenic oil
Zinc oxide	Di-(2-ethylhexyl)-phthalate
Zinc carbonate	**Extenders**
Stearic acid	Silica gel
	Carbon black

Table 17. Chemical Agents Used in Chemical Tire Devulcanization Processes

Triphenyl phosphine
Sodium di-n-butyl phosphite
Thiol-amine reagents (specifically propane-thiol/piperidine, dithiothreitol, and hexane-l-thiol)
Lithium aluminum hydride
Phenyl lithium
Methyl iodide
Hydroxide with quaternary ammonium chloride as a catalyst
Orthodichlorobenzene
Diphenyldisulphide
Diallyl disulfide
Toluene, naphtha, benzene, and/or cyclohexane, etc. in the presence of sodium
Diamly disulfide
Dibenzyl disulfide
Diphenyl disulfide
Bis(alkoxy aryl) disulfides
Butyl mercaptan and thiopenols
Xylene thiols
Phenol sulfides and disulfides
Alkyl phenol sulfides (for SBR)
N,N-dialkyl aryl amine sulfides (for SBR in neutral or alkaline solutions)

Table 18. Potential Types of Chemical Compounds Emitted by Chemical and Ultrasonic Devulcanization Technologies[a]

Compound	Probable Source
Benzene	Plasticizers: Aromatic oil
Methylcyclohexane	Plasticizers: Naphthemic oil
Toluene	Plasticizers: Aromatic oil
Heptane	Plasticizers: Aliphatic oil
4-Vinylcyclohexene	Polymers: Natural Rubber (polyisoprene), styrene-butadiene rubber (SBR), cis-Polybutadiene
Ethylbenzene	Plasticizers: Aromatic oil
Octane	Plasticizers: Aliphatic oil
p-Xylene	Plasticizers: Aromatic oil
Styrene	Polymers: styrene-butadiene rubber (SBR)
Nonane	Plasticizers: Aliphatic oil
1,4-Cyclohexadiene-1-isopropyl-4-methyl	Polymers: Natural Rubber (polyisoprene)
Isopropylbenzene	Plasticizers: Aromatic oil
Cyclohexene-1-methyl-3-(1-methylvinyl)	Polymers: Natural Rubber (polyisoprene)
Propylbenzene	Plasticizers: Aromatic oil
Benzaldehyde	Polymers: styrene-butadiene rubber (SBR)
1-isopropyl-4-methylcyclohexane (trans)	Plasticizers: Naphthemic oil
1-isopropyl-4-methylcyclohexane (cis)	Plasticizers: Naphthemic oil
1-isopropyl-3-methylcyclohexane	Plasticizers: Naphthemic oil
Decane	Plasticizers: Aliphatic oil
Tri-isobutylene	Polymers: styrene-butadiene rubber (SBR) & cis-Polybutadiene; Plasticizers: Naphthemic oil
Cyclohexene-5-methyl-3-(1-methylvinyl)	Polymers: Natural Rubber (polyisoprene)
Indane	Plasticizers: Naphthemic oil
1-Isopropyl-4-methylbenzene	Plasticizers: Aromatic oil
Cyclohexene-1-methyl-4-(1-methylvinyl)	Polymers: Natural Rubber (polyisoprene)
1-Isopropyl-2-methylbenzene	Plasticizers: Aromatic oil
Dimethylstyrene	Polymers: styrene-butadiene rubber (SBR)
Undecane	Plasticizers: Aliphatic oil
Tetramethylbenzene	Plasticizers: Aromatic oil
1,2,3,4-Tetrahydronaphthalene	Plasticizers: Naphthemic oil
1,3-Di-isopropyl benzene	Plasticizers: Aromatic oil
1,4-Di-isopropyl benzene	Plasticizers: Aromatic oil
2-Isopropyl-6-methylphenol	Antioxidents: Alkylphenols

53

Compound	Probable Source
Cyclohexylisothiocyanate	Retarders: n-Cyclohexyl-thiophthalimide
Cyclododecatriene	Polymers: cis-Polybutadiene
Dodecane	Plasticizers: Aliphatic oil
Tridecane	Plasticizers: Aliphatic oil
Tetraisobutylene	Polymers: styrene-butadiene rubber (SBR) & cis-Polybutadiene; Plasticizers: Naphthemic oil
p-ter-Butylstyrene	Polymers: styrene-butadiene rubber (SBR)
Dimethylpropylhexahydronaphthalene	Plasticizers: Naphthemic oil
Tetradecane	Plasticizers: Aliphatic oil
Nonylbenzene	Plasticizers: Aromatic oil
2,6-Di-ter-butyl-p-quinone	Antioxidents: 2,6-Diterbutyl-hydroquinone
Pentadecane	Plasticizers: Aliphatic oil
1,6-dimethyl-4-isopropyl-1,2,3,4-tetra-hydronaphthalene	Plasticizers: Naphthemic oil
Decylbenzene	Plasticizers: Aromatic oil
Di-ter-butylthiophene	Plasticizers: Aromatic oil
Diethyl phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate
Hexadecane	Plasticizers: Aliphatic oil
1,2-Di-tolylethane	Polymers: styrene-butadiene rubber (SBR)
Heptadecane	Plasticizers: Aliphatic oil
2,6-Di-ter-butyl-4-ethylphenol	Antioxidents: Alkylphenols
Octadecane	Plasticizers: Aliphatic oil
1-Phenylnaphthalene	Plasticizers: Aromatic oil
Di-iso-butyl phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate
Tridecylbenzene	Plasticizers: Aromatic oil
Dibutyl phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate
Eicosane	Plasticizers: Aliphatic oil
Heneicosane	Plasticizers: Aliphatic oil
Docosane	Plasticizers: Aliphatic oil
Di-(2-ethylhexyl) phthalate	Plasticizers: Di-(2-ethylhexyl)-phthalate

[a] Information based on types of emissions from the vulcanization area of a tire retreading operation and from a tire retreading extrusion operation.
Source: Cocheo, et al., 1983.

If the chemical agent orthodichlorobenzene is used, chlorinated hydrocarbons could potentially be released in the form of air emissions. Methyl iodide is volatile, and if used as a devulcanization agent, it could be vaporized. Since tire manufacturing utilizes zinc oxide and zinc carbonate, chemical devulcanization might also produce airborne metal particulates.

Once the batch is fully processed, the reactor is vented. The vent gases are treated prior to release to the atmosphere. The vapors cannot be treated by vapor phase carbon because these chemicals will plate out and blind the carbon, making it ineffective. Instead, the vapor from the batch

reactor needs to be thermally oxidized. At the high exit temperatures, typically as high as 2000°F (1100°C), the thermal oxidizer vent gases need to be cooled in a quench tower to approximately 300°F (150°C). Then, to remove any metals or other particulate, the vent gases are piped to a baghouse.

Because of the high thermal oxidizer temperatures, methyl mercaptans (RSH) or hydrogen sulfide (H_2S) from the crumb rubber is oxidized to sulfur dioxide (SO_2). Therefore, downstream of the baghouse, a scrubber is required to remove sulfur dioxide (SO_2), as shown in Figure H. Scrubbed vent gases are then released to the atmosphere.

In addition to the scrubber vent gases described above, liquid waste is generated from the scrubber. This liquid stream contains sodium sulfate (Na_2SO_4). This liquid waste can be disposed in receiving waters such as a river, stream, or bay. However, discharging to receiving waters will require a significant amount of treatment equipment and a permit.

Obtaining the necessary National Pollutant Discharge Elimination System (NPDES) permit is often difficult. NPDES permits are typically costly and require a significant amount of paperwork to be submitted to the Regional Water Boards. The cost and effort to obtain an NPDES permit is considerable, and the time required to receive an approved NPDES permit is lengthy.

If the facility is located near a sanitary sewer, the publicly-owned treatment works (POTW) can conduct treatment of the effluent water. Using the POTW eliminates the need to buy, install, and operate water treatment equipment. Furthermore, it is much simpler to obtain a POTW permit than an NPDES permit because the paperwork, application fee, and time required to obtain the permit is significantly less.

In addition to an application fee, POTWs will assess a usage fee. The fee will be based on the volume of effluent water discharged to their sanitary district and on the difficulty that wastewater treatment will create. Furthermore, the local POTW may not have the capacity and the capability to handle the quantity and composition of chemicals present in the liquid waste.

As seen in Figure H, the devulcanized rubber is moved from the batch reactor to a separator by a heated extruder. Liquid that drips off the devulcanized rubber is removed in the separator and eliminated by feeding it to the same thermal oxidizer as the vent gases from the batch reactor. After the liquid has dripped off the devulcanized rubber in the separator, any remaining moisture is removed in the dryer. Fired dryers are typically fueled by natural gas burners. Dryer vent gases are piped to the common thermal oxidizer.

Based on the concentration of solids in the scrubber effluent, processing the scrubber effluent through a filter press to dewater the solids may be necessary and cost-effective. Filter-pressed dewatered solids are called "filter cake." Filter cake might require disposal in a hazardous waste site. Even though the waste disposal site may accept the scrubber effluent water, the economics may favor installation and use of a filter press. This is necessary to dewater the solids due to the high cost of disposal of liquid waste.

Ultrasonic

Devulcanization by ultrasonic methods may be a continuous process (see Figure I). As the figure illustrates, crumb rubber is loaded into a hopper and is subsequently fed into an extruder. The extruder mechanically pushes and pulls the rubber. This mechanical action serves to heat the rubber particles and soften the rubber.

Figure I. Block Flow Diagram of an Ultrasonic Devulcanization System
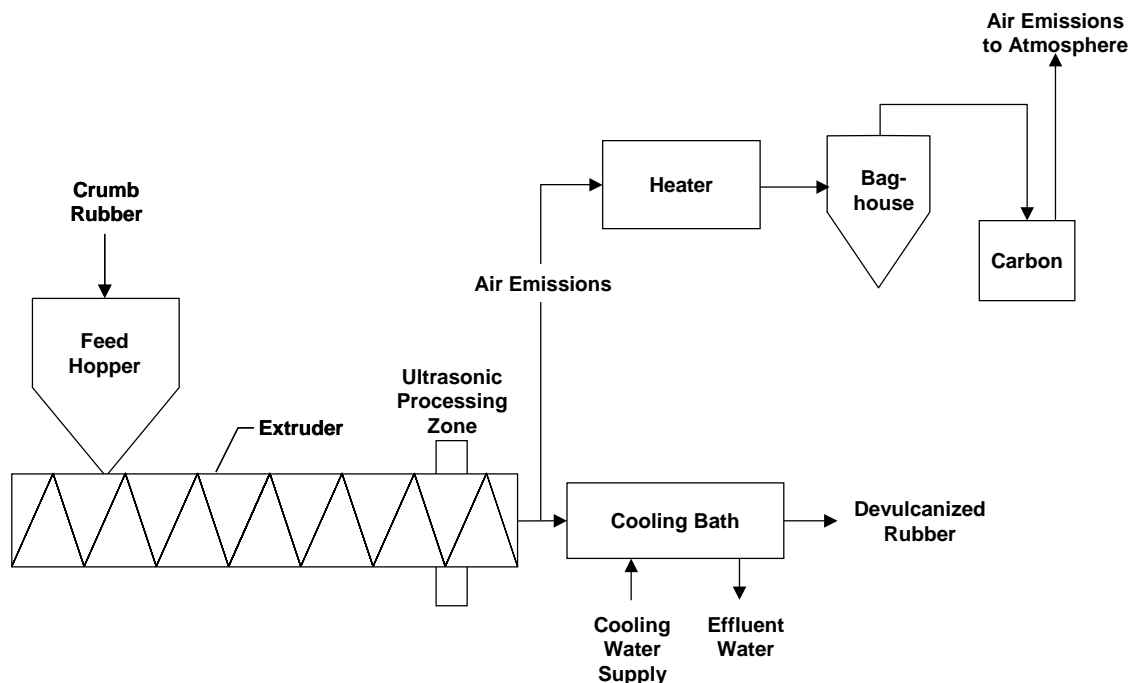
As the softened rubber is transported through the extruder cavity, the rubber is exposed to ultrasonic energy. The resulting combination of ultrasonic energy, along with the heat, pressure, and mechanical mastication, is sufficient to achieve varying degrees of devulcanization. The exposure time to the ultrasonic energy is only seconds. Essentially all of the rubber entering the process is discharged from the extruder in a semi-solid product stream. Process losses would be primarily emissions of fine particulate or of gases, if any, resulting from the mechanical and thermal applications occurring during devulcanization.

Since the typical operating temperature of an ultrasonic devulcanization reactor is about 230°F (110°C), less vapor emission would be expected than from chemical devulcanization. Furthermore, since no chemicals are added to break the sulfur bonds that caused vulcanization to occur, there would likely be lower air emissions. After exiting through the extruder die, the rubber is passed through a cooling bath and then dried. Tire raw materials for this process are listed in Table 16.

Typical types of gaseous compounds that could be released from an ultrasonic devulcanization reactor are listed in Table 18. Vented vapors would need to be treated by one of two methods. One method would be to use a small thermal oxidizer. The design of the thermal oxidizer, baghouse, and scrubber would be similar to that described previously for chemical devulcanization. However, the physical size of the oxidizer would be smaller, and the baghouse and scrubber would be larger.

A second method to treat the vent gases exiting the ultrasonic devulcanization reactor would be use of vapor phase carbon. In this method, due to the lower operating temperatures of the ultrasonic process, vent gas exiting the ultrasonic zone would have to be heated above the dew point temperature. If this elevation in temperature is not accomplished, the vent gases could condense on the surface of the carbon and thus blind the bed. In other words, adsorption sites on the surface of the carbon would be ineffective, and vent gases would exit the carbon bed untreated.

If vapor phase carbon were to be used, the capital cost would be less than that of a thermal oxidizer. However, carbon is not very efficient. Weight loading can be approximately 10 weight percent—in other words, adsorbing ten pounds of vent gas contaminants for every 100 pounds of carbon used. Use of carbon will have a relatively high operating cost. Also, the disposal of spent carbon can be very expensive. This is especially true if the spent carbon requires disposal at a hazardous waste disposal site. Even if the carbon is regenerated on-site, adsorption efficiency decreases after each regeneration. Typically, carbon can only be regenerated ten times. For illustration purposes, Figure I indicates the use of vapor phase carbon.

Devulcanized rubber exiting the ultrasonic processing zone has to be cooled. A common method of reducing the rubber temperature is a cooling bath. The volume of cooling water used would be significant. Cooling water may become contaminated from the process; this effluent water leaving the cooling bath has to be treated. As discussed in the chemical treatment system, a POTW permit would be preferred to obtaining an NPDES permit. If an air cooler such as fin fans is used in lieu of water in the cooling bath, the volume of effluent liquid would be reduced.

Another alternative would be to use a closed-loop cooling system, where the cooling water is cooled and returned to the process for reuse. If there is a buildup of contaminants, a small slip-stream could be taken off and treated in a POTW, greatly reducing the amount of effluent that would otherwise require treatment.

Air Emission Regulations

Regulations controlling air emissions have been written by multiple organizations. The United States Environmental Protection Agency (U.S. EPA) established Title V regulations that apply if the emission rate is for a large facility. Title V emissions are based on Hazardous Air Pollutants (HAP), the federal designation for toxic compounds. U.S. EPA also has regulations governing emission of Volatile Organic Compounds (VOC).

In addition to Federal Regulations set by U.S. EPA, air emission regulations are established by the California Air Resources Board (ARB). ARB has developed a list of chemicals identified as Toxic Air Contaminants (TAC). A copy of the list is included as Appendix B. If a chemical is not listed as a TAC, it can still be listed by ARB as an air toxic under the Air Toxic "Hot Spots" Information Act list of substances. In California, air emission regulations established by local agencies are typically the most stringent. For purposes of this analysis, the regulations of the Bay Area Air Quality Management District (BAAQMD) were reviewed for applicability to devulcanization processes. None of the three agencies appear to have regulations written specifically for waste tire devulcanization.

BAAQMD Regulations

In general, based on the type of gaseous compounds listed in Table 18, a permit would be required for a waste tire devulcanization facility. Regulation 2, Rule 1, section 121.1 allows an exemption from needing a permit for grinding the tires to make crumb rubber, provided that organic emissions from the coolant, lubricants, or cutting oil are 5 tons per year or less. Regulation 2, Rule 1, section 121.10 provides an exemption from needing a permit for the curing of rubber products. The use of mold release products or lubricants is not exempt unless the VOC contents of these materials are less than 10 pounds per year.

BAAQMD categorizes air emissions into six classes of pollutants:

1. Precursor Organic Compounds (POC). This is basically the same as the U.S. EPA VOCs.

2. Non-Precursor Organic Compounds (NPOC). All organics will fall into class 1 or 2.

3. Nitrous oxides (NOx).

4. Carbon monoxide (CO).

5. Particulate matter smaller than 10 micron (PM_{10}).

6. Sulfur dioxide (SO_2).

Regulation 2, Rule 1, section 103 requires that any class of pollutant not exceed 10 pounds on a single day. In addition, the facility cannot exceed 5 tons per year of any class of pollutant. A large emission rate can trigger the need to complete a federal Title V permit, in addition to BAAQMD permits. A Title V permit is required if the facility emits more than 100 tons per year of all six of these classes; or, if the emission rate exceeds 10 tons per year of a single hazardous air pollutant (not all pollutants are HAPs); or, if emission rate exceeds 25 tons per year of just HAPs.

Regulation 2, Rule 1, Table 316 (see Appendix C on page 77) lists trigger levels that cannot be exceeded for specific chemicals.

Regulation 8, Rule 2, section 301 states that it is illegal to discharge into the atmosphere an emission containing more than 15 pounds per day and containing a concentration of more than 300 parts per million total carbon on a dry basis.

If POCs are greater than 10 pounds per day, BAAQMD requires that equipment be in place to treat air emissions. Depending on the type of emission, it could be an electrostatic mist precipitator and a baghouse to control particulate and visible emissions. Scrubbers and thermal oxidizers are commonly used to control organic concentrations in vent gases.

Chapter 7. Barriers

The study has identified a number of potential barriers to developing an economically competitive waste tire devulcanization technology. The barriers are described below under specific subject headings.

Technical Needs

Devulcanization of specific types of rubber and/or waste tire rubber has a long history. However, only recently have limited technical data been reported in the available literature. Usually when reported, the tested properties of devulcanized rubber compose an incomplete list. This is especially true in the interpretation of how the devulcanized product would perform during compounding, in the manufactured end product, or both. Few studies provide detailed descriptions and characteristics of the waste tire feedstock that would be required to evaluate the effect of feedstock properties on system operation and on end product performance.

Clearly, the need for testing of waste tire devulcanization technologies is substantial. These tests should be based on a variety of waste tire feedstocks in order to identify the technical barriers to the technologies (and, therefore, resulting cost barriers). Circumstantial and anecdotal evidence indicates significant technical and economic barriers to devulcanization of waste tire rubber.

If such testing studies are to be productive, they must measure a comprehensive list of material properties, including percent rubber devulcanized (using accepted test methods wherever possible). The tests must fully describe feedstock and system operating conditions. Finally, the tests must relate process operating conditions (including energy required) to properties of devulcanized material and to those of a manufactured end product.

Equipment design parameters must be reported for the various devulcanization processes. These parameters are necessary to provide a basis for determining the capital equipment costs needed for the complete economic analysis required to determine unit prices; for example, $/lb. The parameters are also necessary to determine the technical feasibility of producing a high-quality devulcanized product.

The Cost of Devulcanization

At present, the economic cost of devulcanization technology is a critical barrier to developing and commercializing the process. The price spread between the selling price of crumb rubber and the price of virgin rubber is substantially less than current estimates of devulcanization cost. Crumb rubber is the raw material for the devulcanizing process.

Further aggravating the problem is the expected discount sales price of devulcanized rubber. The properties of devulcanized rubber will probably never equal those of virgin rubber. Based on current estimates, the processing cost must be reduced by 80 to 90 percent (to 10 to 20 percent of current estimates) before the process could be operated profitably. This represents a substantial reduction in the estimated processing cost.

Based on the results of the cost analysis, research and development should be directed toward reducing the cost of devulcanization processes or toward developing lower-cost processes. If the processing cost cannot be substantially reduced, improving the properties of devulcanized waste tire rubber is of limited benefit. This applies also to reducing the cost of existing devulcanization processes and to developing new types of technologies.

The Mixture of Rubber Types Present in a Tire

Because a tire is not a homogeneous product with respect to the type of rubber used, any ground rubber becomes a mixture of all the types of rubber and the compounds in the tire. For example, the sidewalls of a radial tire are predominantly natural rubber. The tread is a compound with SBR and either natural rubber or polybutadiene, and the inner liner is mostly polyisobutylene. Whitewalls are EPDM, and other specialized parts are other types of rubber or special compounds of more than one type.

When a tire is size reduced, the ground rubber becomes a mixture of all types of materials with different properties. Optimizing devulcanization processes is difficult when materials of disparate properties go into the feedstock for the process. Thus, the properties of the resultant devulcanized product are compromised.

Two possible areas of research could be focused on this problem. The first would examine how a tire could be reclaimed in a process that would isolate the different types of rubber. For example, by grinding off the tread, that rubber could be devulcanized separately, with the devulcanized product blended into new tread rubber.

A second option would be to process truck tires separately and then blend this devulcanized rubber back into natural rubber compounds. This would be possible since truck tires contain a much higher proportion of natural rubber. Finally, a third option would be to find applications (most likely non-tire) where the mixture derived from ground tires would have properties adequate for that application. The best way to find such applications would be to compare the measured properties of rubber devulcanized from ground whole tires with the properties required for different types of rubber products. The goal would be to find a match.

Gaining Acceptance in High-Value Markets

Because devulcanization technologies require a feedstock in particulate form, the cost of devulcanization (and, therefore, its product) must include the price of the crumb rubber feedstock. Consequently, devulcanized products cannot compete on price for products manufactured with crumb rubber. Devulcanized waste tire rubber can only be realistically used in high-value applications where crumb rubber cannot be used due to property requirements. This means that the properties of devulcanized waste tire rubber must be sufficiently close to those of virgin rubber so that it can be blended with virgin rubber without substantially reducing the properties of the final compound.

For example, if the devulcanized rubber has a modulus equal to 90 percent of that of virgin rubber, blending it into virgin rubber at a 10 percent rate would probably reduce the modulus of the compound by approximately 1 percent. Before acceptance for use in vehicle tires—where failures could potentially lead to deaths, injuries, and legal action—use of devulcanized tire rubber would have to be subjected to extensive testing. Other markets require high-quality rubber, but the liability risks are not as great as those of the new tire market.

Research and development work should be focused on two areas. First, efforts should continue to bring the properties of the devulcanized material as close as possible to that of virgin rubber. Second, researchers should conduct comprehensive studies of compounding to better quantify the properties of blends containing devulcanized waste tire rubber and virgin rubber.

Market research is also needed in this area to determine requirements for gaining acceptability in tire applications. Second, researchers need to identify non-tire applications where devulcanized rubber has the best chance of finding acceptability.

The Environmental Effects of the Process

The estimates of processing costs developed in this study do not include the costs of pollution control. Chapter 6 of this report, "Environmental Analysis," lists the types of emissions that could be expected. The difficulty of permitting such a process and the cost of compliance with environmental regulations may comprise a significant barrier to the implementation of this technology.

Conceivably, pollution control costs could add 10 to 30 percent to the cost of devulcanization. The difficulty of permitting—and the cost—would be a function of the type of devulcanization technology, the processing rates, and other factors. In general, the expectation is that the cost of environmental control systems for chemical devulcanization systems would be greater than that for ultrasonic or mechanical processes.

Potential research and development efforts on environmental control would include quantifying the environmental releases of various chemical compounds from the process and developing cost-effective means of using or recovering these compounds or their derivatives.

Chapter 8. Conclusions and Recommendations

The key conclusions and recommendations of the study are presented below, under four general headings.

Research and Development

Approximately 25 potential technology researchers and developers have been identified throughout the world and North America, including 3 in California. Apparently, only a very small number of devulcanization systems are now operating. These are primarily small-capacity systems, devulcanizing single types of natural or synthetic rubber (as opposed to devulcanizing rubber from waste tires) or both.

The definition of "devulcanization" varies in the literature. This compromises the ability to identify devulcanization processes, to interpret the performance of devulcanization technologies, and to determine the feasibility of devulcanizing waste tire rubber.

Particle size can play an important role in the effectiveness and feasibility of devulcanization processes. A number of devulcanization processes require a finely sized particle distribution, while others can tolerate or use a coarser particle size. In the process of producing very finely sized rubber, the distinction between or among individual processes of devulcanization, surface devulcanization, and size reduction becomes narrow or blurred. Many of the descriptions of devulcanization technologies are unclear about the relationship between feedstock particle size distribution and performance of particular devulcanization technologies and their devulcanized products.

The composition of rubber and additives that are used in rubber compounds in the manufacture of vulcanized rubber can and do have a dramatic effect on the properties of materials manufactured from devulcanized rubber. Apparently, the inferior properties of some poorly (inadequately) devulcanized rubber can be compensated for by the addition of chemicals and the adjustment of operating conditions, among other remedies. In many cases in the literature, this situation is not addressed or discussed. Consequently, comparing devulcanization technologies is difficult. From most of the literature descriptions of the processes, what happens to the sulfur and other vulcanization chemicals during the various processes is unclear.

Technical

Based on the information collected in the study, CalRecovery believes that the only method of achieving bulk devulcanization, as opposed to surface devulcanization, rests with ultrasonic or microwave devulcanization methods. Of these two methods of energy application, ultrasound appears to have substantially more research and development history. An important observation is that microwave technology is not an effective or efficient way to devulcanize non-polar rubber types, which collectively compose the vast majority of the mass of rubber in waste tires.

Because of the ability to internally devulcanize cured rubber, ultrasonically devulcanized waste tire rubber may have more desirable marketing characteristics than those of surface-devulcanizing processes under similar conditions of cost and yield. The latter processes (surface devulcanizing) include mechanical, chemical, and biological processes. However, test data and applications for ultrasonically devulcanized waste tire rubber are lacking in the industry, along with process cost documentation.

Market

At the present time, the processing cost of the various types of devulcanization process is greater than the difference between the price of crumb rubber (the raw material) and the likely selling price. This price would be at a discount from the price of virgin rubber. The processing cost is the single largest factor limiting the market for devulcanized rubber, so the most potentially productive areas of research are the reduction of processing cost and the development of substantially lower-cost processes. To be viable under current market conditions, the processing cost of devulcanization would have to be reduced by an estimated 50 to 90 percent.

The devulcanized rubber market is most fully developed for single product materials made from manufacturing scrap that are reclaimed for reuse in the same process or in a broader specification application. The reprocessing of single rubbers depends upon being located near a large-volume rubber products company with enough scrap and enough rubber applications to justify the devulcanization step.

Devulcanization of waste tire rubber, despite considerable research and developmental effort, is still in an early growth stage. Devulcanization lacks adequate test data and data interpretation, and it has poorly defined end product specifications without adequately justified and defined applications and uses. Research funds appear to be most available for studying devulcanization of single rubber types, as opposed to studying rubber types with complex mixtures such as those present in waste tires.

Devulcanization typically reduces the resulting rubber product properties and value compared to virgin material. Devulcanized waste tire rubber would normally be expected to sell at a steep discount to virgin rubber, unless special circumstances prevail.

Devulcanized tire rubber yields a product that is effectively a mixture of rubbers, fillers, and chemical additives that create barriers to its reuse as a blending material. In applications already using crumb rubber, devulcanized rubber can have advantages if the process combines a vulcanized rubber or other compatible material to create an integrated structure. The structure must have much better properties than those imparted by the filler role that crumb rubber frequently serves.

While the market prospects are currently limited for devulcanized rubber because of economics, California has both a large supply of crumb rubber and markets for raw materials supporting its large rubber products industry. Creative thinking may offer ways to better match devulcanized tire rubber with potential applications that fit its product profile closely. A better fit would offer a fair value (less substantial discount) for the devulcanized rubber, while still giving the buyer the incentive of a discount off virgin rubber prices.

The devulcanization industry needs a classification method for devulcanized tire rubber based on analytical results and measured properties. The measured properties should include those that characterize the performance of the devulcanized material during the process of compounding as well as the performance of the end product itself.

Potential Future Efforts

If waste tire devulcanization is to succeed in the marketplace, it needs proven applications and a competitive price. Consequently, if the CIWMB is to pursue devulcanization as a method of waste tire management and recycling, program efforts would best be devoted to reducing processing cost and proving viable product applications. In this pursuit, researchers and developers of devulcanization processes should be required to perform comprehensive testing. These tests should evaluate the characteristics of waste tire feedstocks and their resultant effect on

process and end product performance. Equally important is the identification of specific, viable markets and the uses of devulcanized waste tire rubber. Finally, the test data should include documentation of production and marketing costs and the prices users offer for the devulcanized rubber.

Abbreviations and Acronyms

BR	Butadiene rubber
C-C	Carbon-carbon
C-S	Carbon-sulfur
EPDM	Ethylene propylene diene monomer
GRT	Ground rubber tire, or ground tire rubber
NR	Natural rubber
phr	Parts per hundred
RRM	Renewable resource material
SBR	Styrene-butadiene rubber
S-S	Sulfur-sulfur

Appendix A
Support for Cost of Waste Tire
Devulcanization Technologies

Support for Cost of Waste Tire Devulcanization Technologies

Capital	Mechanical	Chemical	Ultrasonic
Equipment	77,141	138,075	135,870
Engineering	14,828	27,615	27,174
Totals	91,969	165,690	163,044
Operations			
Labor	79,560	79,560	79,560
Utilities	6,379	8,393	13,171
Feedstocks[a]	24,960	55,224	19,344
Rent (building)	24,000	28,800	24,000
Totals	134,899	171,977	136,075

[a] Includes crumb rubber feedstock and chemicals, if any.

Financial Assumptions:
- Capital amortization:
  – Interest rate: 6% per annum
  – Amortization period: 20 years
- Labor:
  – Technician: $27/hr, including overhead; 1 FTE
  – Maintenance: $22.5/hr, including overhead; 0.5 FTE
- Electricity: $0.12/kWh
- Chemicals: $0.06/lb tire rubber processed
- Crumb rubber: $0.21, $0.12, and $0.124/lb for Chemical, Mechanical, and Ultrasonic technologies, respectively
- Building rental: $1/ft^2/mo

Appendix B
Toxic Air Contaminant List

Toxic Air Contaminant List Quick Reference Format

December 1999

I. Substances identified as Toxic Air Contaminants by the Air Resources Board, pursuant to the provisions of AB 1807** and AB 2728** (includes all Hazardous Air Pollutants listed in the Federal Clean Air Act Amendments of 1990).

Information within the square brackets refers to the corresponding subcategory on the *Substances By Category* version of the list.

Acetaldehyde [IIa]

Acetamide [IIa]

Acetonitrile [IVa]

Acetophenone [IVa]

2-Acetylaminofluorene [V]

☐ Acrolein [IIa]

Acrylamide [IIa]

Acrylic acid [IIa]

Acrylonitrile [IIa]

Allyl chloride [IIa]

4-Aminobiphenyl [V]

Aniline [IIa]

o-Anisidine [IVa]

Antimony compounds (Note 4) [IIa]

☐ * Inorganic Arsenic and Arsenic compounds (Note 4) [IIa] (inorganic including arsine)

* Asbestos [IIa]

[asbestiform varieties of serpentine (chrysotile) riebeckite (crocidolite), cummingtonite-grunerite(amosite), tremolite, actinolite, and anthophyllite]

* Benzene (including benzene from gasoline) [IIa]

Benzidine [V]

Benzotrichloride [V]

Benzyl chloride [IIa]

Beryllium Compounds (Note 4) [IIa]

Biphenyl [IVa]

Bis(2-ethylhexyl)phthalate (DEHP) [IIa]

Bis(chloromethyl)ether [IIa]

Bromoform [V]

* 1,3-Butadiene [IIa]

* Cadmium and cadmium compounds (Note 4)[IIa] (metallic cadmium and cadmium compounds)

Calcium cyanamide [V]

Caprolactam [V]

☐ Captan [VI]

☐ Carbaryl [VI]

Carbon disulfide [IIa]

* Carbon tetrachloride (Tetrachloromethane) [IIa]

Carbonyl sulfide [IVa]

Catechol [IVa]

Chloramben [V]

Chlordane [V]

* Chlorinated dibenzo-*p*-dioxins and dibenzofurans (Note 5) [IIa] 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) [IIa]

☐ Chlorine [IIa]

Chloroacetic acid [IVa]

2-Chloroacetophenone [V]

Chlorobenzene [IIa]

Chlorobenzilate [IVa]

* Chloroform [IIa]

Chloromethyl methyl ether [V]

Chloroprene [IVa]

☐ Chromium and Compounds (Note 4) [IIa]

* Chromium VI (Hexavalent chromium) [IIa]

Cobalt Compounds (Note 4) [IIa]

Coke Oven Emissions [V]

☐ Cresols/Cresylic acid (isomers and mixture) [IIa]

m-Cresol [VI]

o-Cresol [V]

p-Cresol [V]

Cumene [IVa]

☐ Cyanide compounds (Note 4&11) [IIa]

☐ 2,4-D, salts and esters [VI]

DDE (p,p-Dichlorodiphenyldichloroethylene) [V]

Diazomethane [V]

Dibenzofuran [IVa]

1,2-Dibromo-3-chloropropane (DBCP) [V]

Dibutylphthalate [IVa]

☐ 1,4-Dichlorobenzene (p-Dicholorobenzene) [IIa]

3,3-Dichlorobenzidene [IIa]

Dichloroethyl ether (Bis(2-chloroethyl) ether) [V]

☐ 1,3-Dichloropropene (Telone)[IVa]

☐ Dichlorvos (DDVP) [VI]

Diethanolamine (Note 6) [IIa]

N,N-Diethyl aniline (N,N-Dimethylaniline) [V]

Diethyl sulfate [V]

3,3-Dimethoxybenzidine [V]

4-Dimethyl aminoazobenzene [V]

3,3-Dimethyl benzidine (o-Tolidine) [V]

Dimethyl carbamoyl chloride [V]

Dimethyl formamide [IIa]

1,1-Dimethyl hydrazine [IVa]

Dimethyl phthalate [IVa]

Dimethyl sulfate [IVa]
4,6-Dinitro-o-cresol, and salts [V]
2,4-Dinitrophenol [V]
2,4-Dinitrotoluene [V]
1,4-Dioxane (1,4-Diethyleneoxide) [IIa]
1,2-Diphenylhydrazine [V]
Epichlorohydrin (1-Chloro-2,3-epoxypropane) [IIa]
1,2-Epoxybutane [IIa]
Ethyl acrylate [IVa]
Ethyl benzene [IIa]
Ethyl carbamate (Urethane) [IIa]
Ethyl chloride (Chloroethane) [IIa]
* Ethylene dibromide (1,2-Dibromoethane) [IIa]
* Ethylene dichloride (1,2-Dichloroethane) [IIa]
Ethylene glycol [IIa]
Ethylene imine (Aziridine) [V]
◻ * Ethylene oxide (1,2-Epoxyethane) [IIa]
Ethylene thiourea [IIa]
Ethylidene dichloride (1,1-Dichloroethane) [IIa]
Fine mineral fibers (Note 13) [IVa]
◻ * Formaldehyde [IIa]
Glycol ethers (Note 7) [IIa]
Heptachlor [V]
Hexachlorobenzene [IIa]
Hexachlorobutadiene [V]
Hexachlorocyclopentadiene [V]
Hexachloroethane [IIa]
Hexamethylene-1,6-diisocyanate [IIa]
Hexamethylphosphoramide [V]
Hexane [IIa]
Hydrazine [IIa]
◻ Hydrochloric acid [IIa]
Hydrogen fluoride (Hydrofluoric acid) [IIa]
Hydroquinone [IVa]
Isophorone [IIa]
* Inorganic Lead and Inorganic lead compounds (includes elemental lead) (Note 4 & 8) [IIa]
Lead and compounds (Note 4) [IIa] (does not include elemental lead)
◻ Lindane [IIa]
Maleic anhydride [IIa]
◻ Manganese and compounds (Note 4) [IIa]
Mercury and compounds (Note 4) [IIa]
◻ Methanol [IIa]
◻ Methoxychlor [VI]
Methyl bromide (Bromomethane) [IIa]

Methyl chloride (Chloromethane) [IVa]

Methyl chloroform (1,1,1-Trichloroethane) [IIa]

Methyl ethyl ketone (2-Butanone) [IIa]

Methyl hydrazine [IVa]

Methyl iodide (Iodomethane) [V]

Methyl isobutyl ketone

Methyl isocyanate [V]

Methyl methacrylate [IIa]

Methyl tertiary butyl ether (MTBE) [IIa][IIIa]

4,4-Methylene bis (2-chloroaniline) [IIa]

* Methylene chloride (Dichloromethane) [IIa]

4,4-Methylenedianiline [IIa]

Methylene diphenyl diisocyanate (MDI) [IIa]

Naphthalene [IIa]

* Nickel and compounds (Note 4) [IIa] (metallic nickel & inorganic nickel compounds)

Nitrobenzene [IIa]

4-Nitrobiphenyl [V]

4-Nitrophenol [V]

2-Nitropropane [IIa]

N-Nitroso-N-methylurea [V]

N-Nitrosodimethylamine [IIa]

N-Nitrosomorpholine [IIa]

Parathion [V]

* Particulate emissions from diesel-fueled engines [IIa]

☐ Pentachloronitrobenzene (Quintozene) [IVa]

☐ Pentachlorophenol [IIa]

* Perchloroethylene (Tetrachloroethylene) [I]

Phenol [IIa]

p-Phenylenediamine [IVa]

Phosgene [IIa]

Phosphine [IIa]

☐ Phosphorus [IIa]

Phthalic anhydride [IIa]

Polychlorinated biphenyls (PCBs) [IIa]

Polycyclic organic matter (POM) (Note 9) [IIa][IIIa][IVa] Benzo[a]pyrene (Note 10) [IIa]

1,3 Propane sultone [Iia]

beta-Propiolactone [V]

Propionaldehyde [IVa]

☐ Propoxur (Baygon) [VI]

Propylene dichloride (1,2-Dichloropropane) [IVa]

☐ Propylene oxide [IIa]

1,2-Propylenimine (2-Methyl aziridine) [IVa]

Quinoline [V]

Quinone [V]

Radionuclides (including radon) (Note 12) [IVa]
Selenium and compounds (Note 4) [IIa]
Styrene [IIa] [IIIa]
Styrene oxide [IIa]
1,1,2,2-Tetrachloroethane [IIa]
Titanium tetrachloride [IVa]
Toluene [IIa]
2,4-Toluene diamine (2,4-Diaminotoluene) [V]
Toluene-2,4- diisocyanate [IIa]
o-Toluidine [V]
Toxaphene (Chlorinated camphene) [V]
1,2,4-Trichlorobenzene [IVa]
1,1,2-Trichloroethane [IIa]
* Trichloroethylene [IIa]
2,4,5-Trichlorophenol [V]
2,4,6-Trichlorophenol [IIa]
Triethylamine [IIa]
☐ Trifluralin [VI]
2,2,4-Trimethylpentane [IVa]
Vinyl acetate [IIa]
Vinyl bromide [V]
* Vinyl chloride [IIa]
Vinylidene chloride (1,1-Dichloroethylene) [IIa]
☐ Xylenes (isomers and mixture) [IIa]
m-Xylene [IIa]
o-Xylene [IIa]
p-Xylene [IIa]

II. Substances NOT identified as Toxic Air Contaminants, known to be emitted from stationary source facilities, which are being evaluated for entry into Category I. Factors considered in this evaluation include carcinogenic and noncarcinogenic health effects, emissions and exposure in California. Aluminum and Compounds (Note 4) [IVb]

Ammonia [IIb]
Ammonium nitrate [IVb]
Ammonium sulfate [IVb]
Barium and Compounds (Note 4) [IVb]
Benzoyl chloride [IVb]
Bis(2-ethylhexyl)adipate [IVb]
Bromine and compounds (inorganic) (Note 4) [IVb]
Butyl acrylate [IVb]
☐ n-Butyl alcohol [IVb]
sec-Butyl alcohol [IVb]
tert-Butyl alcohol [IVb]
Butyl benzyl phthalate [IVb]

Carbon black and Carbon black extracts [IVb]
Chlorinated fluorocarbons [IVb]
☐ Chlorine dioxide [IIb]
Chlorophenols [IVb]
☐ Chloropicrin [IIb]
☐ Copper and Compounds (Note 4)[IIb]
☐ Creosotes [IIb]
Crystalline silica [IIIb]
Cumene hydroperoxide [IVb]
Cyclohexane [IVb]
Decabromodiphenyl oxide [IVb]
Dialkylnitrosamines [IVb]
Diaminotoluene (mixed isomers) [IVb]
Dicofol [IVb]
Environmental Tobacco Smoke (Note 14) [IVb]
☐ Ethylene [IIb]
Gasoline vapors [IVb]
☐ Glutaraldehyde [IVb]
Hexachlorocyclohexanes [IIb]
Hydrogen sulfide [IIb]
☐ Isopropyl alcohol [IIb]
4,4'-Isopropylidenediphenol [IVb]
Michler's ketone [IIb]
Molybdenum trioxide [IVb]
Nitric acid [IIb]
Nitrilotriacetic acid [IVb]
Peracetic acid [IVb]
☐ 2-Phenylphenol [IVb]
☐ Phosphoric acid [IIb]
Propene [IVb]
☐ Silver and Compounds (Note 4) [IIb]
☐ Sodium hydroxide [IIb]
☐ Sulfuric acid [IIb]
Terephthalic acid [IVb]
Thiourea [IVb]
☐ 1,2,4-Trimethylbenzene [IVb]
☐ Zinc and Compounds (Note 4) [IIb]

Footnotes

* Substances which have already been identified by the Air Resources Board as Toxic Air Contaminants through a comprehensive AB 1807 risk assessment and which have health values developed by the Office of Environmental Health Hazard Assessment and approved by the Scientific Review Panel. A full risk assessment report is available.

** AB 1807, Statutes 1983, chapter 1047, Health & Safety Code sections 39650 et. seq.
AB 2728, Statutes 1992, chapter 1161, Health & Safety Code sections 39655 et. seq.

☐ To be listed as a Toxic Air Contaminant, these substances will go though a comprehensive AB 1807 risk assessment. These substances are active ingredients in pesticides in California. For further information regarding the pesticidal uses of these compounds, please contact the Department of Pesticide Regulation.

Note 4: For all listings above which contain the word "compounds" and for glycol ethers, the following applies: Unless otherwise specified, these listings are defined as including any unique chemical substance that contains the named chemical (i.e, antimony, arsenic, etc.) as part of that chemical's infrastructure.

Note 5: Chlorinated dibenzo-*p*-dioxins and dibenzofurans: The cancer potency value for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was determined for the identification of chlorinated dioxins and dibenzofurans as toxic air contaminants in 1986. At that time, the Board identified dibenzo-*p*-dioxins and dibenzofurans chlorinated in the 2,3,7, and 8 positions and containing 4,5,6, or 7 chlorine atoms as toxic air contaminants. Since 1986, International Toxicity Equivalency Factors (ITEFs) have been developed which are used to evaluate the cancer risk due to exposure to samples containing mixtures of chlorinated dibenzo-*p*dioxins and dibenzofurans. ITEFs are numerical factors that express the toxicity of an individual chlorinated dibenzo-*p*-dioxin or dibenzofuran relative to the toxicity of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. ITEFs are listed for 16 chlorinated dibenzo-*p*-dioxins and dibenzofurans.

Note 6: Diethanolamine: There is a 1997 draft report by the National Toxicology Program that shows evidence of carcinogenic activity in mice. (This may result in a change of the cancer classification.)

Note 7: Glycol ethers: Includes mono- and di-ethers of ethylene glycol, diethylene glycol, and triethylene glycol

(R(OCH CH) -OR' where 2 2 n

n = 1,2 or 3

R = alkyl or aryl groups

R = R,H, or groups which, when removed, yield glycol ethers with the structure; R(OCH CH) -OH. Polymers are excluded from the glycol category. 2 n

Note 8: Inorganic Lead: Due to information on non-cancer health effects showing no identified threshold, no Reference Exposure Level has been developed. However, guidelines for assessing noncancer health impacts are currently being developed by ARB staff.

Note 9: Polycyclic organic matter: Includes organic compounds with more than one benzene ring, and which have a boiling point greater than or equal to 100°C.

Note 10: Benzo[a]pyrene: Potency Equivalency Factors (PEF) have been developed for 24 polycyclic aromatic hydrocarbons (PAHs). Using benzo[a]pyrene as a reference compound, a weighting scheme for PAHs was developed in the 1994 Air Resources Board document entitled, *Benzo[a]pyrene as a Toxic Air Contaminant*. When a specific potency value is developed for a chemical, it should be used in place of the PEF.

Note 11: Cyanide compounds: X'CN where X=H' or any other group where a formal dissociation may occur. For example, KCN or Ca(CN)2.

Note 12: Radionuclides: A type of atom which spontaneously undergoes radioactive decay.

Note 13: Fine mineral fibers: Includes mineral fiber emissions from facilities manufacturing or processing glass, rock, or slag fibers (or other mineral derived fibers) of average diameter 1 micrometer or less.

Note 14: Environmental tobacco smoke: An AB 1807-type of health assessment for Environmental Tobacco Smoke was conducted by the Office of Environmental Health Hazard Assessment (OEHHA) and was approved by the Scientific Review Panel on June 19, 1997. The Air Resources Board accepted the report from OEHHA on October 23, 1997 and then forwarded to the Department of Health Services' Tobacco Control Program for appropriate action.

Appendix C
Toxic Air Contaminant Trigger Levels

Toxic Air Contaminant Trigger Levels

Table 2-1-316, Bay Area Air Quality Management District, August 1, 2001

* This is a chemical compound group. If a CAS number is listed, it represents only a single chemical within the chemical class (for metallic compounds, the CAS number of the elemental form is listed; for other compounds, the CAS number of a predominant compound in the group is given).

n/a—No CAS number is available for this compound or compound group.

Compound	CAS Number	Trigger Level (lb/year)
Acetaldehyde	75070	7.2E+01
Acetamide	603505	9.7E+00
Acrolein	107028	3.9E+00
Acrylamide	79061	1.5E-01
Acrylonitrile	107131	6.7E-01
Allyl chloride	107051	3.3E+01
Aminoanthraquinone, 2	117793	2.1E+01
Ammonia	7664417	1.9E+04
Aniline	62533	1.2E+02
Arsenic and arsenic compounds (inorganic)	7440382*	2.5E-02
Asbestos	1332214	3.0E-03
Benzene	71432	6.7E+00
Benzidine (and its salts)	92875*	1.4E-03
Benzyl chloride (see chlorotoluenes)	100447	3.9E+00
Beryllium and beryllium compounds	7440417*	1.4E-02
Bis(2-chloro-ethyl)ether	111444	2.7E-01
Bis(chloro-methyl)ether	542881	1.5E-02
Bromine and bromine compounds (inorganic)	7726956*	3.3E+02
Butadiene, 1,3-	106990	1.1E+00

Compound	CAS Number	Trigger Level (lb/year)
Butyl alcohol, tert-	75650	1.4E+05
Cadmium and cadmium compounds	7440439*	4.6E-02
Carbon disulfide	75150	1.4E+04
Carbon tetrachloride	56235	4.6E+00
Chlorinated dibenzodioxins and dibenzofurans (TCDD equivalent)	1746016*	1.2E-06
Chlorinated paraffins	*	7.7E+00
Chlorine	7782505	1.4E+03
Chlorobenzene	108907	1.4E+04
Chlorofluorocarbons	*	1.4E+05
Chloroform	67663	3.6E+01
Chloro-o-phenylenediamine, 4-	95830	4.2E+01
Chlorophenol, 2-	108430	3.5E+03
Chloro-o-toluidine, p-	95692	2.5E+00
Chloropicrin	76062	3.3E+02
Chloroprene	126998	1.9E+03
Chlorotoluenes	100447*	2.3E+03
Chromium (hexavalent) and chromium (hexavalent) compounds	18540299*	1.3E-03
Copper and copper compounds	7440508*	4.6E+02
Cresidine, p-	120718	4.4E+00
Cresol	1319773	3.5E+04
Cupferron	135206	3.1E+00
Diaminoanisole,	2,4- 96128	2.9E+01
Dibromo-3-chloropropane, 1,2- (DBCP)	96128	9.7E-02
Dichlorobenzene, 1,4-	106467	1.8E+01

Compound	CAS Number	Trigger Level (lb/year)
Dichlorobenzidene, 3,3'-	91941	5.6E-01
Dichloroethane, 1,1-	75343	1.2E+02
Dichloroethylene, 1,1- (see vinylidene chloride)		
Diesel exhaust particulate matter	n/a	6.4E-01
Diethylaminoethanol	100378	2.1E+04
Diethylhexylphthalate (DEHP)	117817	8.1E+01
Dimethylaminoazobenzene, p-	60117	1.5E-01
Dimethylamine	124403	3.8+02
Dimethyl phthalate	131113	2.3E+03
Dinitrotoluene, 2,4-	121142	2.1E+00
Dioctyl phthalate	117840	2.3E+03
Dioxane, 1,4-	123911	2.5E+01
Epichlorohydrin	106898	8.3E+00
Ethyl acetate	141786	6.6E+05
Ethyl acrylate	140885	9.3E+03
Ethyl chloride	75003	1.9E+06
Ethylene dibromide (1,2-dibromoethane)	106934	2.7E+00
Ethylene dichloride (1,2-dichloroethane)	107062	8.7E+00
Ethylene oxide	75218	2.1E+00
Ethylene thiourea	96457	1.5E+01
Formaldehyde	50000	3.3E+01
Freons (see Chlorofluorocarbons)		
Glutaraldehyde	111308	3.3E+02
Glycol Ethers:		
2-Ethoxy ethanol (cellosolve;	110805	3.9E+04

Compound	CAS Number	Trigger Level (lb/year)
ethylene glycol monoethyl ether)		
2-Ethoxyethyl acetate (cellosolve acetate; ethylene glycol monoethyl ether acetate)	111159	1.3E+04
2-Methoxy ethanol (methyl cellosolve; ethylene glycol monomethyl ether)	109864	3.9E+03
2-Methoxyethyl acetate (methyl cellosolve acetate; ethylene glycol monomethyl ether acetate)	110496	1.1E+04
2-Butoxy ethanol (Butyl cellosolve; ethylene glycol monobutyl ether)	111762	3.9E+03
Hexachlorobenzene	118741	3.9E-01
Hexachlorocyclohexanes	58899*	1.8E-01
Hexachlorocyclopentadiene	77474	4.6E+01
Hydrazine	302012	3.9E-02
Hydrogen bromide (hydrobromic acid)	10035106	4.6E+03
Hexane, n-	110543	8.3E+04
Hydrogen chloride	7647010	1.4E+03
Hydrogen cyanide	74908	1.4E+04
Hydrogen fluoride	7664393	1.1E+03
Hydrogen sulfide	7783064	8.1E+03
Isocyanates:		
Methylene-bis-phenyl isocyanate	101688	1.8E+01
Methyl isocyanate	624839	7.0E+01
Toluene diisocyanates	26471625*	1.8E+01
Isophorone	78591	6.6E+04
Isopropyl alcohol	67630	4.4E+05
Lead, inorganic, and lead	7439921*	1.60E+01

Compound	CAS Number	Trigger Level (lb/year)
compounds		
Maleic anhydride	108316	4.6E+02
Manganese and manganese compounds	7439965*	7.7E+01
Mercury and mercury compounds (inorganic)	7439976*	5.8E+01
Methyl alcohol (methanol)	67561	1.2E+05
Methyl bromide	74839	1.2E+03
Methyl chloroform (1,1,1-TCA)	71556	6.2E+04
Methyl mercury	593748	1.9E+02
Methyl methacrylate	80626	1.9E+05
Methylene bis (2-chloroaniline), 4,4'-	101144	4.4E-01
Methylene chloride	75092	1.9E+02
Methylene dianiline, 4,4'-	101779*	4.2E-01
Methylethylketone (MEK)	78933	1.5E+05
Methylpyrrolidone, N-	872504	1.8E+05
Michler's ketone	90948	7.7E-01
Naphthalene	91203	2.7E+02
Nickel and nickel compounds	7440020*	7.3E-01
Nitric acid	7697372	2.3E+03
Nitrobenzene	98953	3.3E+02
Nitropropane, 2-	79469	3.9E+03
Nitrosodiethylamine, N-	55185	1.9E-02
Nitrosodimethylamine, N-	62759	4.2E-02
Nitroso-n-dibutylamine, N-	924163	1.6E-03
Nitrosodiphenylamine, N-	86306	7.3E+01
Nitrosodiphenylamine, p-	156105	3.1E+01

Compound	CAS Number	Trigger Level (lb/year)
Nitroso-N-methylethylamine, N-	10595956	3.1E-02
Nitroso-morpholine, N-	59892	1.0E-01
Nitroso-piperidine, N-	100754	7.1E-02
Nitrosodi-n-propylamine, N-	621647	9.7E-02
Nitrosopyrrolidine, N-	930552	3.3E-01
PAHs (including but not limited to):	*	
Benz[a]anthracene	56553	4.4E-02
Benzo[b]fluoroanthene	205992	4.4E-02
Benzo[k]fluoroanthene	205823	4.4E-02
Benzo[a]pyrene	50328	4.4E-02
Dibenz[a,h]anthracene	53703	4.4E-02
Indeno[1,2,3-cd]pyrene	193395	4.4E-02
PCBs (polychlorinated biphenyls)	1336363*	6.8E-03
Pentachlorophenol	87865	3.8E+01
Perchloroethylene (tetrachloroethylene)	127184	3.3E+01
Phenol	108952	8.7E+03
Phosgene	75445	1.8E+02
Phosphine	7803512	1.9E+03
Phosphoric acid	7664382	4.6E+02
Phosphorus (white)	7723140	1.4E+01
Phthalic anhydride	85449	1.4E+06
Potassium bromate	7758012	1.4E+00
Propane sultone, 1,3-	1120714	2.7E-01
Propylene oxide	75569	5.2E+01
Selenium and selenium compounds	7782492*	9.7E+01

Compound	CAS Number	Trigger Level (lb/year)
Sodium hydroxide	1310732	9.3E+02
Styrene monomer	100425	1.4E+05
Tetrachloroethane, 1,1,2,2-	79345	3.3E+00
Tetrachlorophenols	25167833*	1.7E+04
Tetrahydrofuran	109999	2.7E+05
Toluene	108883	3.9E+04
Toluene diisocyanate, 2,4-	584849	1.8E+01
Thioacetamide	62555	1.1E-01
Toluene diisocyanate, 2,6-	91087	1.8E+01
Trichlorobenzene, 1,2,4-	120821	1.8E+04
Trichloroethane, 1,1,1- (see Methyl chloroform)		
Trichloroethane, 1,1,2- (vinyl trichloride)	79005	1.2E+01
Trichloroethylene	79016	9.7E+01
Trichlorophenol, 2,4,6-	88062	9.7E+00
Urethane (ethyl carbamate)	51796	6.6E-01
Vapam (sodium methyldithiocarbamate)	137428	2.2E+04
Vinyl chloride	75014	2.5E+00
Vinylidene chloride	75354	6.2E+03
Xylenes	1330207*	5.8E+04
Zinc and zinc compounds	7440666*	6.8E+03

Bibliography

Adhikari, B., D. De, and S. Maiti, "Reclamation and Recycling of Waste Rubber," *Progress in Polymer Science*, Vol. 25, No. 7, September 2000, pp. 909–948.

American Chemical Society, Inc., "Rubber Recycling Symposia 1999–2003, Papers presented at the Meetings of the Rubber Division, ACS, Recycling Symposia," July 2003.

American Rubber Technologies <www.americantire.com> (January 2004).

Arastoopour, H. et al., "Process for Recycling of Rubber Materials," U.S. Patent 5,904,885, Illinois Institute of Technology (assignee), May 18, 1999.

Assessment of Markets for Fiber and Steel Produced From Recycling Waste Tires, California Integrated Waste Management Board, Publication No. 622-03-010, Sacramento, Calif., August 2003.

Baker, T.E., "Evaluation of the Use of Scrap Tires in Transportation Related Applications in the State of Washington," Washington Department of Transportation, August 2003.

Benko, D.A. and R.N. Beers, "Surface Devulcanization of Cured Rubber Crumb," U.S. Patent 6,380,269, Goodyear Tire & Rubber Company (assignee), April 30, 2002.

Benko, D.A. and R.N. Beers, "Surface Devulcanization of Cured Rubber Crumb," U.S. Patent 6,387,965, The Goodyear Tire & Rubber Company (assignee), May 14, 2002.

Benko, D.A. and R.N. Beers, "Surface Devulcanization of Cured Rubber Crumb," U.S. Patent 6,462,099, The Goodyear Tire & Rubber Company (assignee), October 8, 2002.

Bilgili, E., H. Arastoopour, and B. Bernstein, "Analysis of Rubber Particles Produced by the Solid State Shear Extrusion Pulverization Process," *Rubber Chemistry & Technology*, Vol. 73, No. 2, May–June 2000, pp. 340–355.

Bilgili, E., H. Arastoopour, and B. Bernstein, "Pulverization of Rubber Granulates Using the Solid-State Shear Extrusion (SSSE) Process: Part I. Process Concepts and Characteristics," *Powder Technology*, Vol. 115, No. 3, April 2001, pp. 265–276.

Bilgili, E., H. Arastoopour, and B. Bernstein, "Pulverization of Rubber Granulates Using the Solid-State Shear Extrusion Process: Part II. Powder Characterization," *Powder Technology*, Vol. 115, No. 3, April 2001, pp. 277–289.

Bilgili, E., B. Berstein, and H. Arastoopour, "Solid State Shear Extrusion of Rubber Granules, American Institute of Chemical Engineers (AIChE) Symposium Series 95 (321), 1999, pp. 83–89.

Bilgili, E., et al. "A New Recycling Technology: Compression Molding of Pulverized Rubber Waste in the Absence of Virgin Rubber," *Journal of Elastomers and Plastics*, Vol. 35, No. 3, 2003, pp. 235–256.

Boron, T., et al, "Applied Research on Ultrasonic Devulcanization of Crumb Rubber," presented at the 156th Meeting of the American Chemical Society Rubber Division, Orlando, Fla., Paper #136, September 1999.

Boron, T., P. Roberson, and W. Klingensmith, "Ultrasonic Devulcanization of Tire Compounds," *Tire Technology International 1996*, 1996, pp. 82–84.

Bowers, B., D. Barber, and R. Allinger, "Profile of Silicone Reclaim," presented at the 130th Meeting of the American Chemical Society Rubber Division, Atlanta, Ga., Paper #81, Fall 1986.

Bredberg, K., "Sulphur-Utilizing Microorganisms in Biotechnological Applications—Rubber Recycling and Vanadium Reduction," Lund University Dissertation Abstracts <www.lub.lu.se/cgi-bin/show_diss.pl/tec_653.html> (September 2003).

Bredberg, K., et al., "Microbial Detoxification of Waste Rubber Material by Wood-Rotting Fungi," *Bioresource Technology*, Vol. 83, No. 3, July 2002, pp. 221–224.

Bryson, J.G., "Reclaim Oil for Digester Process for Rubber Reclaiming," U.S. Patent, 4,148,763, The Goodyear Tire & Rubber Company (assignee), April 10, 1979.

CalRecovery, Inc., *Assessment of Markets for Fiber and Steel Produced From Recycling Waste Tires*, Final Report, prepared for California Integrated Waste Management Board, August 2003.

Christiansson, M., et al., "Reduction of Surface Sulphur Upon Microbial Devulcanization of Rubber Materials," *Biotechnology Letters*, Vol. 20, No. 7, July 1998, pp. 637–642.

Cocheo, V., M.L. Bellomo, and G.G. Bombi, "Rubber Manufacture: Sampling and Identification of Volatile Pollutants," *American Industrial Hygiene Association Journal*, Vol. 44, No. 7, July 1983, pp. 521–527.

Cundell, A.M. and A.P. Mulcock, "The Effect of Curing Agent Concentration on the Microbiological Deterioration of Vulcanized Natural Rubber," *International Biodeterioration Bulletin*, Vol. 9, No. 4, 1973, pp. 91–94.

Cundell, A.M., A.P. Mulcock, and D.A. Hills, "The Influence of Antioxidants and Sulphur Level on the Microbiological Deterioration of Vulcanized Rubber," *Rubber Journal*, Vol. 155, 1973, pp. 22–35.

De, D., B. Adhikari, and S. Maiti, "Reclaiming of Rubber by a Renewable Resource Material. Part 1. Reclaiming of Natural Rubber Vulcanizates," *Journal of Polymeric Materials*, Vol. 14, 1997, pp. 333–342.

De, D., et al., "Reclaiming of Rubber by a Renewable Resource Material (RRM). Part 5. Assessment of Reclaiming of Natural Rubber. Polybutadiene Rubber Blends and Comparison With Commercial Reclaim Rubber," *Polymer Recycling*, Vol. 4, No. 3, 1999, pp. 151–161.

De, D., S. Maiti, and B. Adhikari, "Reclaiming of Rubber by a Renewable Resource Material— Assessment of Vulcanized SBR Reclaiming Process," *Kautschuk Gummi Kunststoffe*, Vol. 53, 2000, pp. 346–351.

Diao, B., A.I. Isayev, and V. Yu. Levin, "Basic Study of Continuous Ultrasonic Devulcanization of Unfilled Silicone Rubber," *Rubber Chemistry & Technology*, Vol. 72, No. 1, March– April 1999, pp. 152–164.

Diao, B., et al., "Surface Behavior of Blends of SBR With Ultrasonically Devulcanized Silicone Rubber," *Journal of Applied Polymer Science*, Vol. 69, 1998, pp. 2691–2696.

Enikolopian, N.S., "Some Aspects of Chemistry and Physics of Plastic Flow," *Pure & Applied Chemistry*, Vol. 57, 1985, pp. 1707–1711.

Findians Oy, "Marketing International Products in Finland," p. 7,
<www.netppl.fi/~findians/finmarket.html> (November 2003).

Fix, S.R., "Microwave Devulcanization of Rubber," *Elastomerics*, Vol. 112, No. 6, 1980,
pp. 38–40.

Fliermans, C.B., and G.G. Wicks, "Combination Biological and Microwave Treatments of Used
Rubber Products," U.S. Patent 6,407,144, Westinghouse Savannah River Company, LLC
(assignee), April 4, 2000.

Franta, I. (ed.), *Elastomers and Rubber Compounding Materials: Manufacture, Properties and
Applications (Studies in Polymer Science)*, Elsevier, New York, 1989.

Fukumori, K., et al., "Recycling technology of tire rubber," Society of Automotive Engineers of
Japan, Inc. (JSAE), *JSAE Review*, Vol. 23, 2002, pp. 259–264.

General Imports, United States International Trade Commission, 1997–2002.

Ghose, S. and A.I. Isayev, "Recycling of Unfilled Polyurethane Rubber Using High Power
Ultrasound," *Journal of Applied Polymer Science*, Vol. 88, No. 4, April 2003, pp. 980–
989.

Gonzalez-de Los Santas, E.A., et al., "Devulcanization of Guayule Rubber by Ultrasound,"
Rubber Chemistry & Technology, Vol. 72, No. 5, November–December 1999, p. 854.

Harshaft, A.A., "Solid Waste Treatment Technology, *Environmental Science & Technology*, Vol.
6, No. 5, May 1972, pp. 412–421.

Holst, O., B. Stenberg, and M. Christiansson, "Biotechnological Possibilities for Waste Tyre-
Rubber Treatment," *Biodegradation*, Vol. 9, No. 3–4, 1998, pp. 301–310.

Hong, C.K., and A.I. Isayev, "Continuous Ultrasonic Devulcanization of Carbon Black-Filled NR
Vulcanizates," *Journal of Applied Polymer Science*, Vol. 79, 2001, pp. 2340–2348.

Hong, C.K., and A.I. Isayev, "Continuous Ultrasonic Devulcanization of NR/SBR Blends,"
Journal of Applied Polymer Science, Vol. 83, 2002, pp. 160–168.

Howlett, J., "LandStar, Inc.," J. Howlett & Associates, Inc., July 1, 1999, p. 5.

Hunt, L.K., and R.R. Kovalak, "Devulcanization of Cured Rubber," U.S. Patent 5,891,926, The
Goodyear Tire & Rubber Company (assignee), April 6, 1999.

International Rubber Study Group, *Rubber Statistical Bulletin*, London, 1982–2003.

International Specialty Products, "Polymer Data 1848,"
<www.ispcorp.com/products/elastomers/content/products/masteroilstain/1848.html> p. 2
(July 2004).

Isayev, A.I., inventor, "Continuous Ultrasonic Devulcanization of Vulcanized Elastomers," U.S.
Patent 5,258,413, The University of Akron, Akron, Ohio (assignee), November 2, 1993.

Isayev, A.I. and J. Chen, "Continuous Ultrasonic Devulcanization of Vulcanized Elastomers,"
U.S. Patent 5,284,625, The University of Akron, Akron, Ohio, (assignee), February 8,
1994.

Isayev, A.I., J. Chen, and A. Tukachinsky, "Novel Ultrasonic Technology for Devulcanization of
Waste Rubbers," *Rubber Chemistry & Technology*, Vol. 68, 1995, pp. 267–280.

Isayev, A.I., S.H. Kim, and V. Yu. Levin, "Superior Mechanical Properties of Reclaimed SBR With Bimodal Network," *Rubber Chemistry & Technology*, Vol. 70, 1997, pp. 194–201.

Kawabata, N., T. Murakami, and S. Yamashita, "Reclamation of Vulcanized Rubber by Chemical Degradation. XII Reclamation of Vulcanized Synthetic IR by the Copper (I) Chloride-Tributylamine Systems," *Nippon Gomu Kyokaishi*, Vol. 52, No. 12, 1979, pp. 768–773.

Kawabata, N., B. Okuyama, and S. Yamashita, "Reclamation of Vulcanized Rubber by Chemical Degradation. XV Degradation of Vulcanized Synthetic Isoprene by the Phenylhydrazine-Iron (II) Chloride System," *Journal of Applied Polymer Science*, Vol. 26, 1981, pp. 1417–1419.

Keursten, G.T.G., and P.H. Groenevelt, "Biodegradation of Rubber Particles in Soil," *Biodegradation*, Vol. 7, 1996, pp. 329–333.

Khait, K., "New Used Tire Recovery Process for Value-Added Products," presented at 145th Meeting of the American Chemical Society Rubber Division Meeting, Chicago, Ill., Paper #24, Spring 1994.

Khait, K., and J.M. Torkelson, "Solid-State Shear Pulverization of Plastics: A Green Recycling Process," *Polymer-Plastics Technology & Engineering*, Vol. 38, 1999, pp. 445–457.

Kleps, T., M. Piaskiewicz, and W. Parasiewicz, "The Use of Thermogravimetry in the Study of Rubber Devulcanization," *Journal of Thermal Analysis Calorimetry*, Vol. 60, No. 1, 2000, pp. 271–277.

Klingensmith, W., "Best Practices in Scrap Tires and Rubber Recycling," published by RETAP (The Recycling Technology Assistance Partnership, a program of CWC [The Clean Washington Center, Seattle, Wash.]), November 1996, p. BP-T2-04-03, <www.cwc.org/tire_bp/T2-04-03.htm>.

Klingensmith, W., "Recycling, Production and Use of Reprocessed Rubbers," *Rubber World*, Vol. 203, 1991, pp. 16–21.

Klingensmith, W., and K. Baranwal, "Recycling of Rubber: An Overview," *Rubber World*, Vol. 218, No. 3, 1998, pp. 41–46.

Knorr, K., "Reclaim From Natural and Synthetic Rubber Scrap for Technical Rubber Goods," *Kautchuk Gummi Kunststoffe*, Vol. 47, No. 1, 1994, pp. 54–57.

Knorr, K., "Reclaimed Rubber: Are Our Technical Abilities at the End?" presented at 148th Meeting of the American Chemical Society Rubber Division Meeting, Cleveland, Ohio, Paper #5, Fall 1995.

Kohler, R., and J. O'Neill, "New Technology for the Devulcanization of Sulfur-Cured Scrap Elastomers," *Rubber World*, Vol. 216, No. 2, 1997, pp. 32, 34–36.

Kyoto Chemical Research Institute, "Chemical Recycling of Sulfur-Cured Natural Rubbers Using Supercritical Carbon Dioxide," September 2002.

LaGrone, B.D., "Reclaiming of Elastomers," *Conservation and Recycling*, Vol. 9, No. 4, 1986, pp. 359–361.

LandStar Rubber, <www.landstarrubber.com/> (January 2004).

Leyden, J.J., "Cryogenic Processing and Recycling," *Rubber World*, Vol. 203, No. 6, March 1991, pp. 28–29.

Loffler, M., G. Straubhe, and E. Straube, "Biohydrometallurgical Technologies: Proceedings of an International Biohydrometallurgy Symposium," Vol. 2, presented at Biohydrometallurgical Symposium, Jackson Hole, Wyo., August 1993, p. 673.

Lynch, J. and B. LaGrone, "Ultrafine Crumb Rubber," presented at 130th Meeting of American Chemical Society Rubber Division, Atlanta, Ga., Paper #37, October 1986.

Makarov, V.M. and V.F. Drozdovski, *Reprocessing of Tyres and Rubber Wastes*, Ellis, Horwood, N.Y., 1991.

Myers, R.D., et al., "Rubber Devulcanization Process," U.S. Patent, 5,602,186, Exxon Research & Engineering Company (assignee), February 11, 1997.

Novotny, D.S., et al, "Microwave Devulcanization of Rubber," U.S. Patent 4,104,205, The Goodyear Tire & Rubber Company (assignee), August 1, 1978.

Okuda, M. and Y. Hatano, Japanese Patent Application 62,121,741, 1987.

Rader, C.P. (ed.), "Plastic, Rubber and Paper Recycling," American Chemical Society, Washington, D.C., 1995.

Recycle Research Institute, *2002 Scrap Tire and Rubber Users Directory*, 2002.

Romine, R.A., and L.J. Snowden-Swan, "Method for the Addition of Vulcanized Waste Rubber to Virgin Rubber Products," U.S. Patent 5,597,851, Battelle Memorial Institute (assignee), January 28, 1997.

R.T. Vanderbilt Co., Inc., *Vanderbilt Rubber Handbook*, 13th Edition, Norwalk, Conn., 1990.

Rubber Manufacturers Association, "Scrap Tire Characteristics," <www.rma.org/scrap_tires/scrap_tire_markets/scrap_tire_characteristics/>, p.1 (January 2004).

Rubberworks International, "Future Projects," <www.rubberworks.net/future.htm>, p.1 (January 2004).

Ruhman, A.A., et al., "Magnetostriction-Based Ultrasound in Rubber Devulcanization and Related Processes," U.S. Patent 6,545,060, Redwood Rubber LLC (assignee), October 5, 2000.

Sato, S., et al., "DeVulcanization of Polyisoprene Rubbers by Wood Rot Fungi," Czech Chemical Society, International Union of Pure and Applied Chemistry, 42nd Microsymposium of P.M.M., Prague, Czech Republic, July 2003, <www.imc.cas.cz/sympo/42micros/poster1.htm>, Paper No. P09 (September 2003).

Schaefer, R., "Processing and Utility of Butyl Reclaim," presented at 130th Meeting of the American Chemical Society Rubber Division Meeting, Atlanta, Ga., Paper #79, October 1986.

Schaefer, R., and R. Berneking, "Natural Rubber Reclaim," presented at 130th Meeting of the American Chemical Society Rubber Division Meeting, Atlanta, Ga., Paper #80, October 1986.

Sekhar, B.C., and V.A. Kormer, European Patent Application, EP 0 690 091 A1, 1995.

Shim, S.E., and A.I. Isayev, "Effects of the Presence of Water on Ultrasonic Devulcanization of Polydimethylsiloxane," *Journal of Applied Polymer Science*, Vol. 88, No. 11, June 2003, pp. 2630–2638.

Shim, S.E., S. Ghose, and A.I. Isayev, "Formation of Bubbles During Ultrasonic Treatment of Cured Polydimethylsiloxane," *Polymer*, Vol. 43, No. 20, September 2002, pp. 5535–5543.

Shim, S.E., et al., "NMR Relaxation and Pulsed Gradient NMR Diffusion Measurements of Ultrasonically Devulcanized Poly (dimethylsiloxane)," *Journal of Physical Chemistry B*, Vol. 106, No. 46, 2002, pp. 12072–12078.

Straube, G., et al., "Method for Reprocessing Scrap Rubber," U.S. Patent, 5,275,948, Holzemann Metallverarbeitung GmbH (assignee), January 4, 1994.

Sunthonpagasit, N., and H.L. Hickman, Jr., "Manufacturing and Utilizing Crumb Rubber From Scrap Tires," *MSW Management*, Vol. 13, No. 7, November/December 2003, pp. 68–70.

Suslick, K.S., *Ultrasound: Its Chemical, Physical and Biological Effects*, Verlag Chemie International, New York, 1988.

Szilard, J.A., *Reclaiming Rubber and Other Polymers*, Noyes Data Corporation, London, 1973.

Tapale, M., and A.I. Isayev, "Continuous Ultrasonic Devulcanization of Unfilled NR Vulcanizates," *Journal of Applied Polymer Science*, Vol. 70, No. 10, December 1998, pp. 2007–2019.

Thomas, A.C., "ReVived Rubber® Technology (RRT)," American Rubber Technology <www.americantire.com/>, pp. 1–3 (January 2004).

Tires2Oil, Inc. <www.tires2oil.com/html/key_features.html> (March 19, 2004).

Tsuchii, A., and K. Takeda, *Applied Environmental Microbiology*, Vol. 56, 1990, p. 269.

Tsuchii, A., T. Suzuki, and K. Takeda, *Applied Environmental Microbiology*, Vol. 50, 1985, p. 965.

Tsuchii, A., K. Takeda, and Y. Tokiwa, *Biodegradation*, Vol. 7, 1997, p. 405.

Tukachinsky, A., D. Schworm, and A.I. Isayev, "Devulcanization of Waste Tire Rubber by Powerful Ultrasound," *Rubber Chemistry & Technology*, Vol. 69, 1996, pp. 92–103.

Ultramer, Inc., "Ultramer Innovations in Polymers," <www.ultramer.com/>, p. 1 (January 2004).

U.S. Department of Commerce, *NAICS 3262 Rubber Products Manufacturing*, 1997 Economic Census, 1997.

Verbruggen, M.A.L., et al., "Mechanisms Involved in the Recycling of NR and EPDM," *Rubber Chemistry & Technology*, Vol. 72, No. 4, September–October 1999, pp. 731–740.

Warner, W.C., "Methods of Devulcanization," *Rubber Chemistry & Technology*, Vol. 67, 1994, pp. 559–566.

Westinghouse Savannah River Company, LLC, <www.srs.gov/general/busiops/tech-transfer/techbrif/TB0007 BioWave.pdf> (March 19, 2004).

Williams, G.R., "The Biodeterioration of Vulcanized Rubbers," *International Biodeterioration*, Vol. 22, No. 4, 1986, pp. 307–311.

Xingru, L., "Activating-Modification Technology and its Application to Rubber Industry," presented at 4th International Symposium on East Asian Resources of Reclaimed Resources Recycling Technology, September 1–4, 1997, Kunming, China.

Yashin, V.V., and A.I. Isayev, "A Model for Rubber Degradation Under Ultrasonic Treatment: Part II. Rupture of Rubber Network and Comparison With Experiments," *Rubber Chemistry & Technology*, Vol. 73, No. 2, May–June 2000, pp. 325–339.

Yu. Levin, V., S.H. Kim, and A.I. Isayev, "Effect of Crosslink Type on the Ultrasound Devulcanization of SBR Vulcanizates," *Rubber Chemistry & Technology*, Vol. 70, 1997, pp. 641–649.

Yu. Levin, V., S.H. Kim, and A.I. Isayev, "Vulcanization of Ultrasonically Devulcanized SBR Elastomers," *Rubber Chemistry & Technology*, Vol. 70, 1997, pp. 120–128.

Yu. Levin, V., et al., "Ultrasound Devulcanization of Sulfur Vulcanized SBR: Crosslink Density and Molecular Mobility," *Rubber Chemistry & Technology*, Vol. 69, 1996, pp. 104–114.

Yun, J., and A.I. Isayev, "Recycling of Roofing Membrane Rubber by Ultrasonic Devulcanization," *Polymer Engineering & Science*, Vol. 43, April 2003, pp. 809–821.

Yun, J., and A.I. Isayev, "Superior Mechanical Properties of Ultrasonically Recycled EPDM Rubber," *Rubber Chemistry & Technology*, Vol. 76, No. 1, March–April 2003, pp. 253–270.

Yun, J., J.S. Oh, and A.I. Isayev, "Ultrasonic Devulcanization Reactors for Recycling of GRT: Comparative Study," *Rubber Chemistry & Technology*, Vol. 74, No. 2, May–June 2001, pp. 317–330.

Yushanov, S.P., A.I. Isayev, and S.H. Kim, "Ultrasonic Devulcanization of SBR Rubber: Experimentation and Modeling Based on Cavitation and Percolation Theories," *Rubber Chemistry & Technology*, Vol. 71, No. 2, May–June 1998, pp. 168–190.

Yushanov, S.P., A.I. Isayev, and V. Yu Levin, "Percolation Simulation of the Network Degradation During Ultrasonic Devulcanization," *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 34, 1996, pp. 2409–2418.

Background Information

Fimrite, D. E., "Recycled Rubber market Opportunities," LandStar Rubber, <www.landstarrubber.com> pp. 46 (January 2004).

International Institute of Synthetic Rubber Producers, *The Synthetic Rubber Manual, 14th Edition*, Houston, January 1999.

Ishiaku, U.S., C.S. Chong, and H. Ismail, "Determination of optimum De-Link R concentration in a recycled rubber compound," *Polymer Testing*, Vol. 18, No. 8, 1999, pp. 621–633.

Milani, M., et al., "Model Compound Studies of the Devulcanization of Rubber via Phase Transfer Catalysis," *Polymer Reaction Engineering*, Vol. 9, No. 1, 2001, pp. 19–36.

Oh, S.J., A.I. Isayev, and M.A. Rogunova, "Continuous ultrasonic process for in situ compatibilization of polypropylene/natural rubber blends," *Polymer*, Vol. 44, No. 8, 2003, pp. 2337–2349.

Recycle Research Institute, *2001 Scrap Tire and Rubber Users Directory*, 2001.

Ultrasonic

Hong, C.K., and A.I. Isayev, "Ultrasonic Devulcanization of Unfilled SBR Under Static and Continuous Conditions," *Rubber Chemistry & Technology*, Vol. 75, No. 1, March–April 2002, pp. 133–142.

Isayev, A.I., "Recycling of Elastomers" *Encyclopedia of Materials: Science and Technology*, K.H.J. Buschow, (ed.), Elsevier Science Ltd., Amsterdam, Vol. 3, 2001, pp. 2474–2477.

Isayev, A.I., "Rubber Recycling" *Rubber Technologist's Handbook*, J.R. White and S.K. De, (ed.), RAPRA Technology Ltd., U.K., 2001, pp. 511–547.

Isayev, A.I., et al., "Modeling of Ultrasonic Devulcanization of Tire Rubbers and Comparison With Experiments," *Plastics, Rubber and Composites Processing and Applications*, Vol. 25, No. 1, 1996, pp. 1–12.

Isayev, A.I., et al., "Ultrasonic Devulcanization of Waste Rubbers: Experimentation and Modeling," *Rheologica Acta*, Vol. 35, No. 6, 1996, pp. 616–630.

Isayev, A.I., S.P. Yushanov, and J. Chen, "Ultrasonic Devulcanization of Rubber Vulcanizates. I. Process Model," *Journal of Applied Polymer Science*, Vol. 59, No. 5, January 1996, pp. 803–813.

Isayev, A.I., S.P. Yushanov, and J. Chen, "Ultrasonic Devulcanization of Rubber Vulcanizates. II. Simulation and Experiment," *Journal of Applied Polymer Science*, Vol. 59, No. 5, January 1996, pp. 815–824.

Johnston, S.T., et al., "Ultrasound Devulcanization of SBR: Molecular Mobility of Gel and Sol," *Rubber Chemistry & Technology*, Vol. 70, 1997, pp. 183–193.

Shim, S.E., and A.I. Isayev, "Ultrasonic Devulcanization of Precipitated Silica-Filled Silicone Rubber," *Rubber Chemistry & Technology*, Vol. 74, No. 2, May–June 2001, pp. 303–316.

Shim, S.E., A.I. Isayev, and E. von Meerwall, "Molecular Mobility of Ultrasonically Devulcanized Silica-Filled Poly (dimethyl siloxane)," *Journal of Polymer Science: Part B: Polymer Physics*, Vol. 41, 2003, pp. 454–465.

Yashin, V.V., and A.I. Isayev, "A Model for Rubber Degradation Under Ultrasonic Treatment: Part I. Acoustic Cavitation in Viscoelastic Solid," *Rubber Chemistry & Technology*, Vol. 72, No. 4, September–October 1999, pp. 741–757.

Yun, J., et al., "Comparative Analysis of Ultrasonically Devulcanized Unfilled SBR, NR and EPDM rubbers," *Journal of Applied Polymer Science*, Vol. 88, No. 2, April 2003, pp. 434–441.